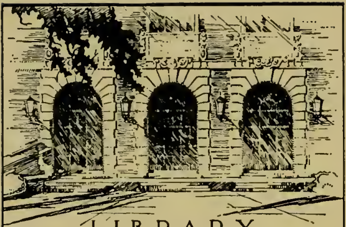

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AMERICAN
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Contributions from the Sheffield Laboratory of Yale College.

XIV.—ON SOME REDUCTIONS WITH ZINC AND AMMONIA.

BY W. G. MIXTER.

Zinc and a solution of an ammonium salt, the nitrate excepted, and zinc with iron or platinum and ammonia water, evolve hydrogen. The reaction has been long known, but has been little used for reducing nitro bodies or for adding hydrogen. If finely divided zinc be placed in aqueous or alcoholic ammonia, and a little platinum chloride solution be added, hydrogen will come off slowly for a long time. The platinum precipitates on the zinc and the two metals form a galvanic couple. The small amount of ammonium chloride present doubtless hastens the action. If an alcoholic solution of a halogen or nitro organic compound be added the action increases, and the mixture often becomes warm. Metnitraniline, dinitrobenzene, dinitrotoluene and nitrotoluidine were each dissolved in alcohol, and some strong ammonia, a liberal quantity of pulverized zinc[1] and a little platinum solution were added. The result of each experiment was a substance which blackened on exposure to the air. Nitrobenzene in an alcoholic solution was subjected to the action of platinized zinc and ammonia for several days. After a time red crystals of azobenzene appeared. To the clear solution sulphuric acid was added, and from the precipitate benzidine was separated by means of ammonia.

---

[1] The zinc was pulverized by pouring the molten metal into a mortar and pounding as soon as it had solidified.

Paraazoxyacetanilide.

Paranitracetanilide[1] was dissolved in a flask in about twenty parts of alcohol; from four to ten parts of concentrated ammonia water and from four to ten parts of pulverized zinc were added, and then a few cubic centimetres of platinum chloride solution were poured in. The mixture became warm in a few minutes, and in course of half an hour the azoxyacetanilide appeared as a yellow fibrous mass. After a couple of hours the evolution of gas was less rapid, and the liquid became cold. The flask was shaken occasionally to prevent the zinc from caking together, and was warmed a few times to hasten the action. After not less than three days, the azoxyacetanilide was filtered off, washed with alcohol, and then shaken up with very dilute hydrochloric acid to remove any zinc compounds which may have been present. After filtering again, and thoroughly washing with water, the substance was dissolved in boiling alcohol and filtered hot. The azoxyacetanilide separates as the solution cools in minute hair-like particles, which are thoroughly washed with alcohol. The yield was about one-half the weight of the nitranilide used. The duplicate analyses are of two different preparations of substance, dried first at common temperatures, and lastly at 100° C.

I. 0.4266 gram gave 0.9638 gram of CO_2 and 0.2028 gram of H_2O.

II. 0.3876 gram gave 59.3 cc. of N at 16° C. and 760 mm. pressure.

III. 0.5365 gram gave 1.2077 gram of CO_2 and 0.2570 gram of H_2O.

IV. 0.3722 gram gave 59.8 cc. of N at 25° C. and 758 mm. pressure.

---

[1] The crude nitranilide, obtained by dissolving acetanilide in well cooled fuming nitric acid, was washed with water, and finally with dilute ammonia to remove any phenole bodies. It was then boiled with repeated portions of water, filtered, and the products from cooling the different solutions kept separate. The crystals obtained from the last two or three boilings were paranitracetanilide, which melted at 207° C. and which gave on boiling with potash no orthonitraniline, but paranitraniline. The crude nitranilide yielded by this treatment a small portion of orthonitraniline.

	Calculated for $C_{16}H_{16}N_4O_3$.	I.	II.	III.	IV.
C	61.54	61.61	...	61.39	...
H	5.13	5.28	...	5.32	...
N	17.95	...	18.15	...	18.40

The substance is formed by the removal of three atoms of oxygen from two molecules of nitracetanilide. From the apparent analogy of its formation to that of azoxybenzene from nitrobenzene the compound is paraazoxyacetanilide, having the formula $\begin{matrix}C_6H_4NHC_2H_3ON\\ |\\ C_6H_4NHC_2H_3ON\end{matrix}\!\!>O$. This view is also supported by the facts that the acetyl groups can be replaced by hydrogen and then the N_2O converted into amido groups with the formation of paraphenylenediamine. The paraazoxyacetanilide melts at 275–278° C., has a light golden yellow color, and is sparingly soluble in boiling and very slightly soluble in cold alcohol.

The alcoholic ammonia filtrate from the azoxyacetanilide was poured back into the zinc, and after several days the solution was evaporated. A black residue remained and nothing definite was obtained.[1]

Metanitracetanilide, from metanitraniline and acetyl chloride, yielded on reducing with zinc and ammonia in one experiment a substance which gave analytical results that corresponded closely with the composition of equal molecules of azoxyacetanilide, $C_{16}H_{16}N_4O_3$, and azoacetanilide, $C_{16}H_{16}N_4O_2$. Further investigation may lead to satisfactory results.

Paraazoxyaniline.

Paraazoxyacetanilide dissolves readily in a hot concentrated solution of potash in alcohol, and when part of the alcohol has been boiled off small red crystals separate. After most of the alcohol has been expelled the potash may be washed out with cold water, and the substance after drying at 100° C. is quite pure.

I. 0.5074 gram gave 1.1761 gram of CO_2 and 0.2431 gram of water.

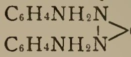
II. 0.2880 gram gave 59.5 cc. of N at 17° C. and 771 mm. pressure.

III. 0.3181 gram gave 66.83 cc. of N at 17° C. and 766 mm. pressure.

---

[1] Since this paper went to press the preparation of azoxyacetanilide has been repeated, and from the alcoholic ammonia filtrate azoacetanilide, $C_{16}H_{16}N_4O_2$, has been separated. It will be described in a future article.

	Calculated for $C_{12}H_{12}N_4O$.	I.	II.	III.
C	63.16	63.21	...	...
H	5.27	5.23	...	...
N	24.56	...	24.78	25.04

The potash effects the replacement of the acetyl group by hydrogen, and assuming that the formula given to the azoxyacetanilide represents its constitution the new body is  $\left.\begin{matrix}C_6H_4NH_2N\\ \vert \\ C_6H_4NH_2N\end{matrix}\right>O$, paraazoxyaniline, a diamido azoxybenzene. It is an analogue of Buckney's azoxytoluidine.[1] Paraazoxyaniline melts at 182–184° C., dissolves rapidly in alcohol, giving a red solution, is sparingly soluble in boiling water, and separates on cooling as a fibrous yellow mass. The hydrochloride crystallizes well from aqueous solution and is sparingly soluble in alcohol. The sulphate separates on adding sulphuric acid to a dilute solution of the azoxyaniline. These two salts are nearly white, tinged with red. The platinum salt was made by adding platinum chloride to a hot alcoholic solution of the hydrochloride. Long brownish red needles separated immediately, which were filtered after cooling and washed with alcohol and dried at 100° C. 0.1712 gram of the salt left after ignition 0.0528 gram of platinum, 30.85 per cent.; theory requires for $C_{12}H_{12}N_4O, H_2PtCl_6$ 30.82 per cent. of platinum. The azoxyaniline is reduced to paraphenylenediamine when heated for several hours to 100° C. with alcoholic ammonium sulphide in a sealed tube. Tin and hydrochloric acid effect the same reduction rapidly. In one experiment the tin was separated as sulphide and the solution was evaporated, and the chlorine in the salt obtained was found to be 39.06 per cent.; theory requires 39.19 per cent. of chlorine in $C_6H_4(NH_2)_2H_2Cl_2$. The phenylenediamine separated from the hydrochloride by distillation with sodium carbonate, Biedermann and Ledoux's method; melted at 140° C.

As azoxybenzene yields azobenzene and hydrazobenzene, we may expect azoxyaniline, which is diamidoazoxybenzene, to be changed by reducing agents to the known substances, diamidoazobenzene and diamidohydrazobenzene. These bodies have, however, not been obtained from the azoxyaniline. In one experiment red azoxyaniline was dissolved in alcoholic ammonia and the solution was then saturated with hydrogen sulphide. After a day the alcohol was boiled off and the dry residue was treated with hot dilute hydrochloric acid, and the solution was filtered from the small quantity of sulphur which remained. The base was precipitated by ammonia, and was dark green. It was dried at 100° C. The analysis shows no change in the composition of the azoxyaniline treated, as described, with ammonium sulphide.

---

[1] Ber. d. deutsch. chem. Gesell. **11**, 1452.

I. 0.4298 gram gave 0.9913 gram of CO_2 and 0.2062 gram of H_2O.

II. 0.3172 gram gave 65 cc. of N at 14° C. and 770 mm. pressure.

	Calculated for $C_{12}H_{12}N_4O$.	I.	II.
C	63.16	62.90	...
H	5.27	5.33	...
N	24.56	...	24.80

This green substance, after recrystallization from boiling water, melted at about 191° C. The hydrochloride and sulphate are green. Its platinum salt, prepared as before described, separated as rather a slimy mass, and after drying had a light grayish tint. It yielded 30.61 per cent. of platinum. Tin and hydrochloric acid reduced the green substance analyzed to paraphenylenediamine. While the color, melting point and the character of its platinum salt indicate that this green substance is a different modification from the azoxyaniline first described, it is probably the same compound colored green by some body formed by the action of the ammonium sulphide. The red azoxyaniline gave on boiling both its aqueous and alcoholic solutions through which a current of sulphur dioxide was passing, green solutions, which did not react for sulphuric acid, an indication that there had been no reduction. The residues left after evaporation were green.

Metaazoxybenzanilide.

20 grams of metanitrabenzanilide, from metanitraniline and benzoyl chloride, were dissolved in 300 cc. of boiling alcohol, and then 200 cc. of alcohol saturated with ammonia; 300 grams of pulverized zinc and 1 gram of platinum in solution were added. Gas was freely evolved, and in half an hour the precipitate was quite thick. After standing twenty-four hours the mixture was heated to boiling, filtered hot, and the substance was digested with a fresh portion of boiling alcohol and washed with alcohol. It was then shaken up with water to remove the zinc particles as much as pos-

sible, and next treated with dilute hydrochloric acid. It was finally washed with water and dried at 100° C. The product was an exceedingly light powder of a pale yellow color.

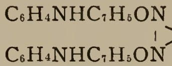
I. 0.4671 gram gave 1.233 gram of CO_2 and 0.2075 gram of H_2O.

II. 0.4168 gram gave 1.1045 gram of CO_2 and 0.1851 gram of H_2O.

III. 0.366 gram gave 39.9 cc. of N at 15° C. and 762 mm. pressure.

	Calculated for $C_{26}H_{20}N_4O_3$.	I.	II.	III.
C	71.56	71.99	72.27	...
H	4.58	4.93	4.93	...
N	12.85	...	...	12.98

The formula



$$\left.\begin{array}{l} C_6H_4NHC_7H_5ON \\ | \\ C_6H_4NHC_7H_5ON \end{array}\right> O$$

represents the constitution of the substance as analogous to that of azoxyacetanilide. The azoxybenzanilide melts at about 272° C. It is insoluble or nearly insoluble in alcohol, ether and benzene. It was treated with a boiling solution of potash in alcohol, and a substance soluble in alcohol was the result; and from the nitrogen found in this substance it appeared that only one benzoyl group had been separated. Warm oil of vitriol dissolves the azoxybenzanilide and sets free benzoic acid, but the product of the reaction was too small for satisfactory investigation.

It may be stated that in the first attempt to prepare the meta-azoxybenzanilide the mixture was exposed to the zinc for several days, and the substance which separated from the solution was treated as already described. Duplicate analyses showed that the reduction had gone further than required for the formation of an azoxy-compound, and indicated a mixture of equal molecules of azoxybenzanilide and azobenzanilide, a result analogous to that obtained in the reduction of the metanitracetanilide. The alcoholic filtrate from the azoxybenzanilide was poured back on to the zinc and left for two or three weeks. No further precipitation took place, and the solution on evaporation left a tarry mass which dissolved readily in boiling water. The crystals which separated on cooling are Bell's compound $C_6H_4NH_2NHC_7H_5O$,[1] as the following results show:

---

[1] Ber. d. deutsch. chem. Gesell. 7, 497.

	Theory.	Found.
C	73·58	73·37
H	5·66	5·56
N	13·30	13·11

The platinum salt yielded 23.03 per cent. of platinum. Bell's salt requires 23.77 per cent. Bell gives the melting point at 125° C. and the writer's preparations melted at 124° C.

The following formulae show the analogy between the derivatives of nitrobenzene and those obtained from the nitranilides.

Nitrobenzene	$C_6H_5NO_2$	Nitracetanilide	$C_6H_4NHC_2H_3ONO_2$
Azoxybenzene	$\begin{array}{l}C_6H_5N \\ \quad\mid \\ C_6H_5N\end{array}\!>O$	Azoxyacetanilide	$\begin{array}{l}C_6H_4NHC_2H_3ON \\ \qquad\qquad\mid \\ C_6H_4NHC_2H_3ON\end{array}\!>O$
		Azoxyaniline	$\begin{array}{l}C_6H_4NH_2N \\ \qquad\mid \\ C_6H_4NH_2N\end{array}\!>O$
Azobenzene	$\begin{array}{l}C_6H_5N \\ \quad\| \\ C_6H_5N\end{array}$		
Hydrazobenzene	$\begin{array}{l}C_6H_5NH \\ \quad\mid \\ C_6H_6NH\end{array}$		
Aniline	$C_6H_5NH_2$	Phenylenediamine	$C_6H_4NH_2NH_2$
		Nitrobenzanilide	$C_6H_4NHC_7H_5ONO_2$
		Azoxybenzanilide	$\begin{array}{l}C_6H_4NHC_7H_5ON \\ \\ C_6H_4NHC_7H_5ON\end{array}\!>O$
		Amidobenzanilide	$C_6H_4NHC_7H_5ONH_2$

The combustions for the carbon and hydrogen estimations were made with copper oxide and completed with oxygen gas; the nitrogen was determined by Dumas' method with the aid of a Sprengel pump and a Schiff azotometer.

XV.—ON THE DISTRIBUTION OF ARSENIC IN A HUMAN BODY.

By R. H. Chittenden.

A recent judicial investigation into the cause of death in a certain case[1] (J. C.) resulted in the finding of sufficient arsenic in the internal organs to warrant the belief that the entire body contained what would ordinarily constitute a fatal dose of this poison. Nearly six months after burial the body was disinterred, weighed, and nearly one-half of the entire muscle and bony tissue removed for further examination: the object being to ascertain the actual amount of arsenic in the whole body, and at the same time to glean all possible facts relative to the distribution of the poison.

It rarely happens that such a complete and exhaustive chemical analysis is called for in judicial investigations, and thus we find on record but few instances where a poison is sought for quantitatively through the entire body; and yet the results of such a search, in the writer's opinion, may be of primary importance in answering some of the questions which the finding of poison in a human body naturally suggests: In what form was the poison taken? How long had it been in the body before death? Was the person habituated to the use of the poison? etc. These are a few of the questions which, in the case of arsenic at least, call for a decisive answer. Improved chemical methods which give us the means of accurately determining even minute quantities of arsenic, and our knowledge of the absorption and elimination of this poison as gleaned by physiological experiments on animals, give us data which ought to enable us in many cases to draw accurate and concise conclusions.

The results obtained in this investigation have therefore seemed of sufficient scientific importance to merit a somewhat detailed description; for however important physiological experiments on animals may be, and however trustworthy the results obtained are to the scientific man, still from a judicial point of view data regarding the relative absorption of poisons, etc., in the human body are of even greater weight and value.

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[1] The body was found floating in the shallow water on a sandy beach. The body bore no evidences of having been long in the water, and a careful autopsy made by Dr. T. M. Prudden failed to reveal the cause of death. Portions of the various internal organs removed at this time were placed in alcohol and preserved separately for chemical analysis.

The method of analysis consisted in oxidizing a weighed amount of the sampled organic matter with nitric and sulphuric acids at elevated temperatures, the arsenic being ultimately obtained and weighed in the metallic state.[1] From the amount of arsenic found in the portion examined, the content of the entire organ or portion of tissue was calculated. The result, when possible, was verified by a duplicate analysis, while in several instances the content of the entire tissue was calculated from the average of two or more determinations. Such of the internal organs as had been placed in alcohol were sampled for analysis by being cut into fine pieces and then ground to a thick paste with the alcohol[2] in a mortar. The sampling of the muscle and bony tissue was effected by the use of pure nitric acid, with the aid of a gentle heat, by means of which the muscle and bones were entirely dissolved. The method of sampling tissue or large organs in this manner, in toxical investigations, particularly for arsenic, has yielded the writer excellent results, since the confirmation of duplicated analyses so obtainable greatly diminishes the possibility of error, and thus adds greater weight to the chemical testimony.

Following are the quantitative results obtained:[3]

Entire stomach[4] *with contents and esophagus.* Weight, 603 grams. (1) 100 grams sampled substance gave .0013 gram metallic arsenic. (2) 106 grams sampled substance gave .00135 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .158 grain.

Entire large and small intestines with contents and alcohol.—Weight, 1471 grams. (1) 200 grams sampled substance gave .0021 gram metallic arsenic. (2) 671 grams sampled substance gave .0122 gram arsenious sulphide. Calculated from No. 1, total arsenious oxide = .314 grain.

Both kidneys. Weight when dried, 83 grams. Entire substance gave .0015 gram metallic arsenic = .029 grain arsenious oxide.

Liver (one-half). Weight with alcohol, 1482 grams.[5] 110 grams sampled substance gave .0004 gram metallic arsenic, total arsenious oxide = .109 grain.

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[1] For full description of process, see this Journal, **2**, 235.

[2] An examination being also made for alkaloid poisons.

[3] It is hardly necessary to state that the arsenic was subjected to all the known tests to prove its identity. Likewise the metallic arsenic weighed was in many cases converted into other known forms and again weighed.

[4] The mucous membrane of the stomach was entirely free from any signs of inflammation.

[5] Weight of liver free from alcohol, 707 grams.

Brain (one-third). Weight with alcohol, 336 grams. (1) 200 grams sampled substance gave .0007 gram metallic arsenic. (2) 136 grams sampled substance gave .0005 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .0255 grain.

Lungs and spleen[1] (two-thirds). Weight moist tissue, 331 grams. (1) 100 grams sampled substance gave .0017 gram metallic arsenic. (2) 131 grams sampled substance gave .0022 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .1146 grain.

Heart (one-fourth). Weight with alcohol,[2] 411 grams. Entire substance gave .0014 gram metallic arsenic = .028 grain arsenious oxide.

Trachea, larynx and tongue. Weight dried tissue, 175 grams. Entire substance gave .004 gram metallic arsenic = .081 grain arsenious oxide.

Diaphragm. Weight dried tissue, 155 grams. Entire substance gave .0005 gram metallic arsenic = .01 grain arsenious oxide.

Total quantity of arsenious oxide found in internal organs:

Stomach and esophagus	.158 grain.
Liver (one-half)	.109 "
Intestines	.314 "
Kidneys	.029 "
Heart (one-fourth)	.028 "
Lungs and spleen (two-thirds)	.1146 "
Brain (one-third)	.0255 "
Trachea, larynx and tongue	.081 "
Diaphragm	.010 "
	.8691 "

The remaining portions of liver, heart, brain, lungs and spleen, not preserved for analysis, would give by calculation the following quantities of arsenic, assuming that the poison was evenly distributed through these various organs:

One-half of the liver	.109 × 1 =	.109 grain.
Three-fourths of the heart	.028 × 3 =	.084 "
Two-thirds of the brain	.025 × 2 =	.050 "
One-third of lungs and spleen	.1146 ÷ 2 =	.0573 "
		.3003 grain.
Arsenious oxide actually found		.8691 "

Total arsenious oxide in internal organs is therefore 1.1694 grain.

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[1] Portions of lungs, heart and spleen were preserved in one jar. The heart with all of the alcohol was examined in one portion, the lungs and spleen in another.

[2] Weight of heart freed from alcohol, 33 grams.

Left arm. Total weight, 1230 grams. (1) 100 grams sampled tissue gave .0004 gram metallic arsenic. (2) 100 grams sampled tissue gave .00035 gram metallic arsenic. (3) 300 grams sampled tissue gave .0011 gram metallic arsenic. Calculated from the average of Nos. 1 and 2, total arsenious oxide = .094 grain.

Right leg (except thigh bone). Total weight, 4650 grams. (1) 100 grams sampled tissue gave .00012 gram metallic arsenic. (2) 100 grams sampled tissue gave .00012 gram metallic arsenic. (3) 400 grams sampled tissue gave .0005 gram metallic arsenic. Calculated from No. 3, total arsenious oxide = .118 grain.

Thigh bone of right leg. Weight of cleaned bone, 216 grams. Entire substance failed to give any arsenic.

Transverse section of body at pelvis, including pelvic bones.— Total weight, 4060 grams. (1) 100 grams sampled tissue gave .0002 gram metallic arsenic. (2) 100 grams sampled tissue gave .00025 gram metallic arsenic. Calculated from the average of these two determinations, total arsenious oxide = .186 grain.

Muscle from breast, right side. Total weight, 510 grams. (1) 200 grams sampled tissue gave .0019 gram metallic arsenic. (2) 310 grams sampled tissue gave .00255 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .098 grain.

Muscle from back, left side. Total weight, 620 grams. (1) 200 grams sampled tissue gave .00565 gram metallic arsenic. (2) 200 grams sampled tissue gave .00565 gram metallic arsenic. (3) 200 grams sampled tissue gave .0056 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .356 grain.

Summary of the Examination of Muscle and Bony Tissue.

	Total weight.		Total As_2O_3.
Left arm	2 lbs.	11¼ oz.	.094 grain.
Right leg, except thigh bone	10	4	.118
Thigh bone		7½	...
Transverse section	8	15½	.186
Muscle from breast	1	2¼	.098
Muscle from back	1	6	.356
	22 lbs.	46½ oz.	.852 grain.
	24	14½	= 398.5 oz.

The entire body, aside from the internal organs, weighed at the time of disinterment 57 pounds = 912 oz. Thus the proportion,

$$398.5 : 912 :: .852 : x = 1.9498 \text{ grains } As_2O_3$$

must give the total amount of arsenious oxide contained in the entire muscle and bony tissue, provided the portions analyzed represent average samples. Naturally care must be taken to avoid an undue proportion of muscle, since this is invariably richer in arsenic than the bones. In the present instance the only question would be in regard to the bones of the trunk and skull, since one of each pair of limbs was analyzed. The transverse section, however, with the heavy pelvic bones and a portion of the spinal column would certainly contain its due proportion of the bones of the trunk. From our work it would appear then that the amount of arsenic present in the body at the time of death, calculated as arsenious oxide, was 3.1192 grains. Of this amount 1.007 grain was actually weighed, while nearly half of the total amount was separated and examined.

Among the many peculiar features of these results there is perhaps no one more striking than the irregular distribution of the arsenic in the muscle tissue. The following table, in which the arsenic is calculated in grains per pound of sampled tissue, plainly shows this:

1 lb.	sampled	thigh bone	contained	.000	grain	As_2O_3
1	"	leg	"	.011	"	"
1	"	transverse sec.	"	.021	"	"
1	"	arm	"	.034	"	"
1	"	muscle from breast		.087	"	"
1	"	muscle from back		.260	"	"

Now in cases of chronic poisoning, or where persons are habituated to the use of arsenic, the regular distribution of the poison through all parts of the muscle tissue is quite noticeable. Thus in a case previously reported[1] the following results were obtained:

1 lb.	sampled	thigh bone	contained	.004	grain	As_2O_3.
1	"	leg	"	.033	"	"
1	"	arm	"	.046	"	"
1	"	transverse sec.	"	.109[2]	"	"
1	"	muscle and ribs, left breast		.063	"	"
1	"	abdominal muscle, right side		.040	"	"

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[1] This Journal, 2, 332.

[2] The increased amount noticed here is undoubtedly due to the fact that the section extended up higher than in the present case; and as the internal organs lay in place in the body for a year and a half, there was undoubtedly more or less diffusion at this point.

In this case, with the exception of the transverse section, the results obtained are within certain limits comparatively constant. There is not that gradual increase from nothing in the bone up to a quarter of a grain per pound in the muscle of the back, as noticed in the case under discussion. This irregular distribution of the poison in tissue of the same kind is certainly indicative of the arsenic having been taken but a short time before death, particularly as in the bone we find none whatever, or at least none in the quantity examined; while, on the other hand, the nearer we approach the great vessels and organs of the body the greater the amount of arsenic in the muscle tissue. The uneven distribution is due, then, presumably to lack of time, while the entire absence of the poison from the portion of bone examined even more strongly excludes the possibility of chronic poisoning.

Again, in cases of chronic poisoning, or where the arsenic has been in the body for some time previous to death, it is customary to find considerable of the poison in the kidneys, since, as is well known, elimination commences very quickly, and continues without interruption until the poison is wholly removed from the body or until death intervenes. In this case, however, the amount of arsenic in both kidneys is but .029 grain, while in the tongue and throat there is nearly three times as much. Once again, the amount of arsenic in the tongue and throat is nearly as much as the amount contained in the entire left arm; results which would hardly be expected in cases where the poison had had sufficient time for even distribution.

In a previous article[1] Johnson and Chittenden called attention to the fact that the form of the poison, viz. whether readily soluble as sodium arsenite, or comparatively insoluble as arsenious oxide, undoubtedly modifies the amount and rate of absorption, particularly by the brain and muscle tissue. This view was based partly on the results obtained by Scolosuboff[2] and by E. Ludwig,[3] and partly on the results of our own toxical examinations and experiments on animals. Thus Scolosuboff, working entirely with sodium arsenite in solution, obtained results all of which agreed in showing that the nerve tissue of the poisoned animal both in acute and chronic cases contains a much larger percentage of arsenic than the muscle tissue or even the liver. Thus in one experiment the brain of a bull-dog fed on sodium arsenite gave per 100 grams tissue .00885 gram metallic arsenic, while the same weight of liver yielded only .00271 and the muscle but .00025 gram metallic arsenic. Scolosuboff's only error was one of theory, in that he assumed what he had found to be true of sodium arsenite to be true also of the more insoluble arsenious oxide, thus producing much confusion on this point. Again it has been recently asserted, without foundation, that the presence or absence of arsenic in the brain is an index as to whether the poison was introduced into the body before or after death. It is undoubtedly true that the finding of arsenic in the brain is an indication amounting almost to proof that the poison was not *post mortem*, since by no ordinary process of diffusion could the arsenic pass such a distance from the alimentary tract, especially in view of the rapid fixation of the poison by conversion into the insoluble sulphide. But on the other hand, in cases of poisoning with arsenious oxide, the absence of arsenic in detectable quantities in the brain in nowise proves, in the writer's opinion, that the poison was not taken prior to death.

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[1] This Journal, **2**, 332.

[2] Bulletin de la Société Chimique de Paris, **24**, 124.

[3] Anzeiger der K. Akad. d. Wissensch. Wien, **18**, 18. See this Journal, **2**, 336-337.

E. Ludwig, of Vienna, from his experience in the examination of human beings poisoned with arsenious oxide, both in acute and chronic cases, as well as from his experiments on dogs, decides that with this form of arsenic the bones and brain contain but a mere trace of the poison, while the liver, as a rule, contains the most arsenic. This view is substantiated by the results from the analysis of the body of Mary Stannard, Mrs. Riddle, and our experiments on animals; for even where large quantities of arsenious oxide have been taken during a period of many days, the amount found in the brain is generally unweighable.

This view being correct, the amount of arsenic found in the brain in the present case admits of but one interpretation. Only one-third of the brain was delivered to the writer for analysis, but this amount contained .025 grain of arsenic, being in the proportion of .034 grain to 1 lb. of brain and alcohol. The only theory then consistent with this result and with the facts at our disposal is that the arsenic was taken in a form readily soluble and diffusible. Again, the large amount of arsenic found in the muscle tissue of the back is not otherwise easily accounted for.

NEW HAVEN, *January* 11, 1883.

HYDRATED CARBON DISULPHIDE.

By F. P. Venable.

This body, discovered by Berthelot[1] and Wartha,[2] has been examined also by Duclaux[3] and by Ballo.[4] The descriptions of it given in our text-books show, however, that our knowledge of it is still somewhat indefinite and incomplete. The following experiments, undertaken at first for the purposes of class illustrations, may serve to clear up some of the doubtful points concerning this body. In filtering carbon disulphide, a sensation of decided cold will be noticed whenever the filter paper is touched. To determine the lowering of temperature caused by the rapid evaporation of the carbon disulphide, a thermometer bulb was wrapped with filter paper, and then suspended over a shallow vessel so that the paper dipped beneath the disulphide contained in it. The mercury sank rapidly to 18° C., and the paper became covered with a peculiar cauliflower-like growth of a snow-white substance, which was seen to be the same as that produced by forcing a current of air across the surface of the disulphide. In further experiments with the thermometer the paper was discarded as uselessly cumbrous, the thermometer was hung just touching the liquid, and evaporation was started by blowing through a tube obliquely into the disulphide so that the little waves struck against the bulb. The formation of the snow-like solid soon commenced. The blowing could then be stopped, and the growth went on rapidly until it had reached a height of 5–6 cm. above the surface. If a current of air was directed upon this growth, it increased most rapidly on the side exposed to the current, forming little tufts resembling miniature, compactly formed, trees, and reaching in some cases a length 7–8 mm. One point observed was that the amount of moisture in the air had a decided effect upon the ease of causing this formation and the rapidity of the growth.

A simple and effective mode of showing as a class experiment the abstraction of heat by the rapid evaporation of the disulphide, or more properly speaking by the formation of the hydrate, is to take a small glass tube with thin walls (such as is used for seed specimens) about 90 mm. long and having a diameter of 10 mm.

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[1] Ann. Ch. Phys. [3] **46**, 490.

[2] Ber. Chem. Ges. **3**, 80.

[3] Bull. Soc. Chim. [2] **8**, 258.

[4] Ber. Chem. Ges. **4**, 118, 160, 294.

This tube is provided with a collar of copper wire having two projecting points which turn easily in the ends, bent into rings, of a strong copper wire attached to a support. The ring of one of the ends of the longer and stouter wire should not be closed, so that the tube can be easily unmounted. This arrangement gives stability, and the tube is much easier to tilt than when simply suspended by threads. The tube is wrapped with a single layer of filter paper for two-thirds its length, the paper extending about 1 cm. beyond the closed end. This lower edge dips just beneath the disulphide when the tube is in position. The tube is filled about half or two-thirds full of water, is placed in its swing, and in a few minutes the water will be frozen and will not flow out when the tube is inverted. In one experiment, with the tube arranged as above, the water was frozen within four minutes. The original temperature of the water was 50° C. and the relative humidity of the surrounding atmosphere was 74 per cent.

Experiments were also made testing the use of the disulphide with Daniell's hygrometer. The bulb had best be enveloped in filter paper, though muslin will do. A watch-glass containing 3–4 cc. of the disulphide is supported beneath it so as just to touch it.

Compared with ether, the reduction of temperature is more rapid and a lower temperature can be reached. At the same time the trouble is less, as the watch-glass once properly placed, the apparatus is self-acting. Of course if impure carbon disulphide is used a yellow deposit of sulphur is left, but this does not interfere except in so far as a neat appearance is concerned. The impure disulphide quickly loses its disgusting odor, and as the formation of the hydrate goes on, only an ethereal odor can be detected, freer from the disagreeable sulphur compounds than even the most carefully purified disulphide. Contrary to the experience of Wartha (*loc. cit.*) no ill effects were felt from breathing air filled with this vapor, although remaining sometimes two or three hours near the shallow glasses in which the evaporation was going on. Of course in a very confined space it might become injurious.

Ballo has recorded one or two experiments to prove that this cauliflower-like growth is a hydrate and not solid frozen carbon disulphide. The following experiment confirms his results, and may be regarded, I think, as conclusive of the dependence of this body for its formation upon the moisture of the air. An open-necked bell-jar, ground, greased, and tightly fitting to a ground glass plate, was provided with a large rubber stopper which was pierced with two holes. Through one of these a calcium chloride tube was inserted, through the other a glass tube with a glass rod working tightly in it and bound to it by means of a piece of rubber tubing so as to be air-tight. The calcium chloride tube was 250 mm. long, and was filled with freshly dried calcium chloride. Inside the bell-jar, a glass acid-holder was filled with fresh concentrated sulphuric acid, and on a triangle placed over it was supported a watch-glass containing carbon disulphide purified by the method of Cloez,[1] and carefully distilled. The glass rod had attached to it by a bit of wax a strip of filter paper 25 mm. broad and 100 mm. long, which had been previously dried in an air-bath for two hours at 100°–105° C. After this was put in the bell-jar, the latter was fitted tightly to the glass plate and the whole allowed to stand about thirty minutes, so that every trace of moisture might be removed from the enclosed air. At the expiration of this time the slip of paper was lowered by the movable rod until it touched the carbon disulphide. The liquid rose rapidly in the pores of the paper, but even after some minutes no sign of the solid incrustations could be seen. As the confined space might have interfered with the evaporation, an aspirator was attached to the calcium chloride tube, but no formation of the solid could be induced. The sulphuric acid was then taken from the jar and water substituted for it. The solid commenced to form almost immediately after the lowering of the paper. The liquid did not rise quite so high as in the first case, and aspirating increased the rate of formation but slightly. If the aspiration was continued until the jar was filled with aqueous vapor, the solid formation suddenly and completely melted away.

Several different ways were tried of forming this hydrate. First, carbon disulphide mixed with about 25 per cent. of water, in a test tube, was placed in a mixture of ice and hydrochloric acid (temperature −23° C.), and for purposes of comparison a tube containing distilled water was placed beside it. The first tube became very milky and turbid, and was frozen to an opaque solid; in the second tube the water remained transparent until completely frozen. A second tube of water and the disulphide was stirred whilst freezing, so as to freeze only on the sides and leave a channel open from bottom to top. All that refused to freeze was poured out, the tube corked and its contents allowed to melt. After melting, a layer of disulphide was observed beneath the water. Of course no great reliance can be placed on such an experiment alone, as the oil may have been mechanically entangled and retained. Again, if a few cc. of carbon disulphide be poured through 2–3 cm. of 90 per cent. alcohol in a tube, the two form clear and distinct layers. Let this tube gently down into a freezing mixture of ice and hydrochloric acid, and the carbon disulphide becomes turbid, while delicate cloud-masses form in the alcohol, and if the alcohol contains more than 10 per cent. water it becames milky and opaque. These cloud-masses disappear above —10° or —9°C., but the temperature could not be accurately fixed, as it seemed to depend upon the amount of carbon disulphide and water held in suspension or solution. If the alcohol and disulphide stand for some time all disulphide apparently settles out, as the cloudiness cannot be again produced by cooling. Care was of course exercised to prevent any agitation or mixing of the liquid layers in sinking the tube into the freezing mixture. A mixture with ether containing a small percentage of water gave also a turbid appearance on being cooled, but the layers were not distinct, nor, on taking the tube from the freezing mixture, did the cloudiness disappear so easily as in the case of the alcohol. Experiments with it then could not be so easily observed nor so rapidly repeated.

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[1] Comptes rendus, **69**, 1356.

The temperature of formation or decomposition given by Wartha (—12° C.) needs additional data to make it correct, according to the following experiments. Even when evaporation and the formation of the hydrate was rapidly going on in a shallow watch glass full of the disulphide, the temperature of the liquid itself did not fall below —6° C. For these experiments a Geissler thermometer graduated to $\frac{1}{10}$ degrees was used, the bulb was nearly spherical, and from its under surface a small bead of glass projected. With this bead touching the surface of the carbon disulphide and the evaporation started by blowing upon it for a short time, the incrustations soon covered the bulb, and the mercury sank rapidly to about —9° C. It then sank very slowly. Seemingly more carbon disulphide was drawn upon the bulb than was used in forming the solid, as the latter had an oily appearance, and this probably tended to keep up the temperature. If the thermometer was raised entirely above the liquid the oily look disappeared, the tufts of solid, before thick and short, branched out and grew stiff and strong, while the mercury rapidly sank to a constant point. To determine this point then the solid was allowed to form over the bulb and some extra disulphide was taken up. By a crank arrangement the thermometer was then raised several inches above the surface of the liquid, and the lowest temperature reached noted. The stay at this point sometimes lasted one or two minutes before the rapid rise commenced. If the thermometer was blown upon whilst the mercury was sinking, the temperature could be reduced several degrees below the point of decomposition. If the constant point had been reached and the mercury was beginning to rise, even if only $\frac{1}{10}$ degree, blowing caused a very rapid rise and melting of the hydrate. The lowest temperature reached by blowing was —19.5° C., the relative humidity of the room being 75. When the thermometer was wrapped with filter-paper and this dipped in the disulphide, the reduction went on regularly to the constant point of decomposition. The slow sinking at —9° C. was not noticed.

Several observations showed that the reduction was in a measure dependent upon the relative humidity of the surrounding atmosphere. This was determined at each observation of the point of decomposition, but the experiments could not be made accurately enough to deduce any fixed law. Air saturated with moisture gave no hydrate. From this point the temperature of decomposition seemed to sink, the lowest points being reached when the air contained between 70 and 80 per cent. of moisture. Below 60 per cent. the temperature in a number of observations rose once more. Even if the current of air was too slight to affect a small candle flame, it would still show upon the delicate thermometer used—the variations caused being shown by shielding the bulb on one side or the other. Entire surrounding and protection of the bulb interfered with the evaporation, and of course the evaporation itself caused currents. Some other way must then be devised for determining this point. Guarding against draughts as carefully as possible, the determinations made, some twenty-five or thirty in all, ranged from —14° C. to —17° C. No point such as that mentioned by Wartha (—12° C.) to which the mercury would rise and remain constant, was observed, the rise being rapid and regular till the temperature of the room was reached.

Berthelot gives the point of decomposition as about —3° C.

University of North Carolina, *February* 10, 1883.

AN ISOPICRAMINIC ACID.

By Charles W. Dabney, Jr.

Some investigations starting from α-metanitrosalicylic acid have led me unexpectedly to an isomer of the well-known picraminic acid.[1] Before entering into the details of the preparation of this new acid and its derivatives, it is necessary to notice the steps by which we have reached the adopted view of the constitution of picraminic acid.

In the first place, picric acid is diorthonitro-paranitro-phenol, counting from hydroxyl as I. This is evident from the fact that it can be produced by nitrating either α-, or orthoparanitrophenol, or β-, otherwise known as diorthonitrophenol.[2]

Secondly, we find that the amido group in picraminic acid is derived from one of the orthonitro groups and not from the paranitro group. Stuckenberg[3] obtained, by nitrating benzoyl-α-amidonitrophenol, derived from paranitroorthoamidophenol, a dinitrobenzoylamidophenol. Stünkel[4] produced independently, by nitrating benzoylorthoamidophenol similarly, a dinitrobenzoylamidophenol, which he proved to be identical with Stuckenberg's phenol. They both gave, by splitting off the benzoyl group, the well-known picraminic acid. Stünkel went further then, and, by getting rid of the amido group in his picraminic acid thus produced by Griess's diazo-reaction, produced again α-dinitrophenol[5] mentioned above, thus putting the question of the constitution of picraminic acid beyond a doubt. Numerous lines of reasoning will lead us to the same constitutional formula, but they are all similar to the argument here cited. Only one other will be mentioned which is entirely different from these.

It is well known that an anhydro compound can only result when the amido group stands in the ortho position, that is, adjoining the OH group. Now, Haarhaus[1] has produced a benzoylpicraminic acid, and made from this, by separating one molecule of water, an anhydro compound, dinitroanhydrobenzoylamidophenol. Stünkel[2] prepared the same from his benzoylpicraminic acid, made, as we saw, from orthoamidophenol.

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[1] The literature of picraminic acid can be briefly given. It was first examined by Wöhler, who produced it by reducing picric acid with ferrous oxide (Pogg. Ann. **12**, 488). Berzelius named it from its color *haematinsalpetersaüre* (Jahr. Ber. **9**, 245). Riecker made the acid by reducing picric acid with hydrogen sulphide, and Girard examined it carefully and called it picraminic acid (Berzelius Lehrb. **4**, 677, and Compt. rend. **36**, 421). Gerhardt suggested first, in his Lehrbuch (**3**, 52), that this was identical with *haematinsalpetersaüre*, and Pugh (Ann. Chem. **96**, 83) and Girard (Compt. rend. **42**, 59) established this as the fact about the same time.

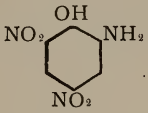
[2] Laurent, Ann. der Chemie, **43**, 219.

[3] Ber. der deutsch. chem. Gesellsch. **10**, 382.

[4] Dissertat. Göttingen, 1880, 15.

[5] Griess had made this from picraminic acid prepared in the ordinary way. Ann. **113**, 210.

We may regard the constitution of the picraminic acid molecule thus as well understood as that of any molecule of this complexity in organic chemistry. It is represented in graphical formula thus:



Prof. Hübner suggested to me at Göttingen in the spring of 1879 to try to introduce a benzoyl group ($—COC_6H_5$) into *α*-metamidosalicylic acid ($C_6H_3COOH, \overset{.}{O}H, NH_2, HCl$), and then to nitrate the product. The suggestion led to the investigations here reported, although the result was entirely different from what was expected.

α-Metanitrosalicylic Acid.—A large amount of this acid was prepared by nitrating salicylic acid according to the method of Hübner.[3] The two nitro acids which are made together by this method were carefully separated. I found the quickest way to accomplish this was to combine the two methods proposed by Hübner. A partial separation was accomplished, handling the isomeric acids in great bulk, by repeatedly dissolving in warm water, in considerably more than the amount necessary to dissolve, and subjecting the solution to a winter's cold. The *α*-nitro acid is considerably less soluble in water below the freezing point than the *β*-nitro acid. Two lots of acids accumulate thus, a dry mass, chiefly *α*-acid, and a liquor, chiefly *β*-acid. Both are converted into their barium salts. Barium *β*-nitrosalicylate is much less soluble in water than the *α*-nitrosalicylate. The dry mass of *α*-acid yields, when converted into barium salts, one small crop of barium *β*-nitrosalicylate crystals, and then only the *α*-nitro salt which is pure when it has been crystallized over twice. The liquor yields several large crops of barium *β*-nitrosalicylate crystals, and finally, upon close concentration, the beautiful bundles of small straw-yellow crystals of barium α-metanitrosalicylate. This salt yielded me the absolutely pure α-metanitrosalicylic acid (melting point 228° C.), which was the starting point for these investigations.

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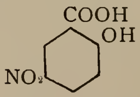
[1] Dissertat. Göttingen, 1880, 22.

[2] *Loc. cit.*

[3] Ann. der Chem. **195**, 7.

The argument for the constitution of this acid is as follows: Kruse[1] obtained from this acid, which is a metanitrohydroxybenzoic acid, as related to benzoic acid, a metanitroorthoamidobenzoic acid, by transforming the OH group into an NH_2 group by means of a well-known reaction. This he then, by getting rid of the NH_2 group (diazo reaction), converted into the familiar metanitrobenzoic acid (melting point 142° C.). It follows from this that the —COOH group and the NO_2 group must stand in the meta relation to each other in the acid under consideration.

As regards the relation of the OH group and the NO_2 group, Hall's[2] work in removing CO_2 from α-metanitrosalicylic acid and producing thereby paranitrophenol (melting point 114° C.), puts this beyond question. They are in the para relation. From these considerations it follows that the —COOH and —OH groups are in the ortho position to each other. This has been verified[3] also by the preparation of salicylic acid or hydroxybenzoic acid by converting the NH_2 in anthranilic acid or orthoamidobenzoic acid into — OH. The acid under examination is, therefore, a metanitroorthohydroxybenzoic acid, and indeed that particular metanitro acid in which the nitro group stands in the para relation to hydroxyl, and which has been called accordingly α-metanitrosalicylic acid. The graphical formula is:



α-Metamidosalicylic Acid.—The amido acid was prepared from the nitro acid by reducing with tin and hydrochloric acid, according to the method described by Schmitt.[4] The amido acid was only fairly stable when hydrochloric acid was left combined with it, C_6H_3, COOH, OH, $NH_2 . HCl$. The free amido acid decomposed almost immediately. Even the solutions of this hydrochloride had to be handled with extreme care. When they had to be evaporated a current of hydrogen sulphide was found to check the destructive oxidation somewhat. α-Metamidosalicylic acid hydrochloride crystallizes in beautiful, long, colorless, glassy-looking needles. They were often obtained an inch long, but were very difficult to get perfectly colorless, being generally brownish, with a film of the oxidation products. Upon heating it decomposes rapidly.

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[1] Dissertat. Göttingen, 1877.

[2] Dissertat. Göttingen, 1875. See also Ann. Chem. **195**, 21-30.

[3] Ann. Chem. **149**; 146.

[4] Zeitschr. für Chemie, 1864, 325.

Introduction of the Benzoyl Group.—The amido acid just described, thoroughly dried and finely ground, was heated with the weighed amount of benzoyl chloride (boiling point 199°C.), counting molecule to molecule, in a flask fitted with a cork and a long tube. Care was taken to banish every trace of water from the apparatus. As the temperature had to be carefully regulated, the flask was heated in a paraffin bath.

The evolution of hydrochloric acids begins as soon as the bath has reached a temperature of 130° C., showing that a reaction is taking place. Conducted at this temperature, the chief product is the compound designated B farther on. In order to get the largest return of the compound desired for the later work—called C below—it was found necessary to heat the bath up to 170–180° C. and maintain it at this for three hours. The mass melts down to a thin liquid and the evolution of hydrochloric acid ceases.

If the bath is heated up to 200° C. or over, the compound formed in largest amount is the one called A below.

I always found a considerable part of the amido acid and benzoyl chloride unchanged, however the mass was treated. Petroleum oils of various densities, chloroform and various other solvents were tried, heating in a sealed tube, without getting any better results. The three compounds A, B and C were formed in every case, although the amounts of each that were formed differed with the temperature at which the reaction was carried out as already indicated.

After a great deal of work I settled upon the following as the best means of separating these three products. The doughy mass was kneaded and washed under hot water until the benzoyl chloride remaining in it was all decomposed and the benzoic acid removed in great part. All of the new compounds are almost completely insoluble in water. In order to get rid of the last of the benzoic acid it was necessary to dissolve the mass in strong acetic acid, precipitate with much hot water and then wash again. The curdy white mass that is left is then dissolved in a warm solution of barium hydrate. The pinkish solution is filtered, and carbon dioxide, free from every trace of mineral acid, is passed through it when cooled. The compound A is precipitated along with the barium carbonate. It is washed first with water, then with dilute acid until the barium is all dissolved out, and can be farther purified by dissolving again in the alkaline solution, precipitating with carbonic acid, etc.

The filtrate contains the barium salts of the compounds B and C. Of these two, the C salt is the less soluble in water, and they can be separated by crystallizing the C salt over and over until it appears in large warty aggregations of short white needles. This salt yields the C acid in a pure form. But the separation can be accomplished quicker by throwing down the acids in the filtrate from the A compound and barium carbonate, with hydrochloric acid, and treating the flocculent precipitate after it has been washed and dried with chloroform. The chloroform dissolves the compound B, and leaves the compound C nearly all behind.

The compounds A, B and C are all alike in being amorphous, or only cryptocrystalline, white substances, and in being little soluble in water. They all dissolve very easily in alcohol. They dissolve easily in acetic acid, though in different amounts. But they leave only a crust or scale when the solvent is removed.

The Compound A only forms salts with an excess of strong alkali. Carbonic acid precipitates it from such solutions. Heated up above 250° C., it turns brown and chars gradually. As I have not been able so far to obtain this compound in a pure form, it was impossible to examine it further. We may have here a mixture of compounds.

The Compound B shows a little more tendency to crystallize. When its chloroform solution is evaporated, it separates in little white grains. After passing through the chloroform solution a number of times it melted regularly and suddenly just when 210° C. was reached. It forms a barium salt which is very soluble in water and does not crystallize well. Treated with strong nitric acid this compound gives a handsome nitro compound. A further notice of this is postponed until it can be more thoroughly examined.

Compound C, α–Benzoylamidosalicylic Acid.—$C_6H_3COOH, OH, NHCOC_6H_5$. Melting point 252° C. The third compound is, as we shall see, the amido acid to which one benzoyl group ($—COC_6H_5$) has been added. Its behavior renders it very probable that its formula is C_6H_3, COOH, OH, $NHCOC_6H_5$ and not C_6H_3COOH, $OCOC_6H_5$, NH_2. The acid is very little soluble in hot water, very easily soluble in pure acetic acid, insoluble in chloroform, benzol and gasoline or naphtha. It was not crystallized. The pure acid, obtained from the barium salt, came down as a white powder from its solution in acetic acid, as this evaporated over caustic potash under a bell-glass. This powder was only cryptocrystalline at best. It melts at 252° C., and forms immediately a dark, tarry-looking liquid. Strong alkalies decompose the solutions of its salts when warm, and cause brown flocculent masses to appear.

ANALYSES.

Carbon and Hydrogen.—I. 0.3231 gram of the acid, separated out of the pure barium salt and dried over sulphuric acid, gave 0.7693 gram carbon dioxide, equal to 0.2098 gram carbon; and 0.1358 gram H_2O, equal to 0.015088 gram hydrogen.

II. 0.3914 gram of the same acid, which was thrown down from the acetic acid solution in addition, gave 0.9429 gram CO_2, equal to 0.25715 gram carbon; and 0.1655 gram H_2O, equal to 0.018388 gram hydrogen.

Nitrogen.—0.2790 gram of the acid, from the barium salt directly, gave 14.0 cc. nitrogen at 15° C. and 735 mm., equal to 0.015849 gram nitrogen.

Calculated for C_6H_3, COOH, OH, $NHCOC_6H_5$.	Found. I.	II.	
$C_{14} = 168 = 65.36$ per ct.	64.93 per ct.	65.70 per ct.	...
$H_{11} = 11 = 4.28$ "	4.67 "	4.70 "	...
$N = 14 = 5.44$ "	... "	...	5.66 per ct.
$O_4 = 64 = 24.92$ "	... "	...	... "

Salts.—*a*-Benzoylmetamidosalicylic acid is a rather strong acid. It would appear from the formula adopted that it is a dibasic acid. The H of hydroxyl and the H of carboxyl might both be substituted by a metal. But its behavior indicates that the second metal atom is at least not stable in the presence of carbonic acid. The only crystallizable salts are those in which *one* H atom is substituted by a metal. When barium hydrate solution is added to a concentrated solution of the monobasic salt, a heavy white precipitate is formed which could not be obtained crystallized. Only the monobasic barium and calcium salts were obtained in sufficiently well-defined form for analysis. The metal salts were all gelatinous precipitates. The copper salt was a light blue-colored jelly; the zinc salt a transparent jelly, etc. The salts of potash and soda were only obtained as a transparent glassy crust when their solutions were evaporated down.

Barium α-benzoylmetamidosalicylate.

$(C_6H_3, OHNHCOC_6H_5, COO)_2Ba + 6H_2O$. This salt is formed when the acid is dissolved in a solution of barium hydrate, and, more slowly, when the acid is boiled in water with barium carbonate. A pinkish solution is formed which deposits brown flocculent masses on evaporation. This brown oxidation's product renders the salt brown or pink at first, but after frequent crystallizations it is obtained in small colorless needles, which group themselves together in large wart-like masses; very easily soluble in water, stable in the air at ordinary temperatures and over sulphuric acid, but loses its water very easily on heating.

Water.—I. 0.5540 gram of the air-dry salt lost only a trace of water over sulphuric acid. Heated up to 120° C. it lost nearly all of its water. Heated continuously at 140° C. it was constant. 0.0810 gram H_2O lost, equal to 14.62 per cent.

II. 0.9508 gram of the air-dry salt lost up to 160° C. 0.1378 gram water, equal to 14.49 per cent.

Calculated for	Found.	
$(C_6H_3,OH,NHCOC_6H_5,COO)_2Ba+6H_2O$.	I.	II.
$H_2O = 14.22$ per cent.	14.62 per cent.	14.49 per cent.

Barium.—I. 0.4268 gram of the water-free salt gave 0.0870 gram $BaSO_4$, equal to 21.01 per cent. barium.

II. 0.6293 gram of the water-free salt gave 0.2282 $BaSO_4$, equal to 21.28 per cent. barium.

Calculated for	Found.	
$(C_6H_3, OH, NHCOC_6H_5COO)_2Ba$.	I.	II.
$Ba = 21.10$ per cent.	21.01 per cent.	21.28 per cent.

Calcium α-benzoylmetamidosalicylate.

$(C_6H_3, OH. NHCOC_6H_5, COO)_2Ca$. This salt is formed in similar manner as the barium salt. As the warm concentrated solution cools down, the very soluble, little, blunt needles crystallized out. They have a fine satin lustre when dry.

Water?—0.5058 gram of the air-dry salt lost, under a bell glass over strong sulphuric acid, 0.0020 gram only, and heated up to 170° C. it lost in weight only 0.0035 gram more. Whether the salt loses all of its water of crystallization in the process of removing the moisture (lying on porous paper in the atmosphere of a heated room), or whether it has *no* water of crystallization, could not be decided. The salt did not appear to change in any respect from the moment the adhering water was removed.

Calcium.—I. 0.1958 gram of the salt, dried at 170° C., gave 0.0480 gram calcium sulphate, equal to 7.18 per cent. calcium.

II. 0.2104 gram of the air-dried salt gave 0.0512 gram calcium sulphate, equal to 7.12 per cent. calcium.

Calculated for $(C_6H_3, OH, NHCOC_6H_5, COO)_2Ca$.	Found. I.	 II.
Ca = 7.24 per cent.	7.18 per cent.	7.12 per cent.

The behavior of this acid when treated with nitric acid renders it almost certain, as we shall see, that its constitution is as written above. Just three different compounds are conceivable as resulting immediately from the entrance of the benzoyl group into α-metamidosalicylic acid.

(1) The acid we have just described agrees with the formula $C_6H_3, OH, NHCOC_6H_5, COOH$. (Compound C.)

(2) $C_6H_3, OCOC_6H_5, NH_2, COOH$.

(3) $C_6H_3OCOC_6H_5, NHCOC_6H_5, COOH$. The compounds A and B, mentioned above, may correspond to the formulas (2) and (3). This remains to be ascertained.

Treatment of α-Benzoylmetamidosalicylic Acid with Nitric Acid, Benzoylparamidodinitrophenol. — $C_6H_2OH, (NO_2)_2NHCOC_6H_5$. Melting point 250° C. Considerable difficulty was experienced at first in the effort to nitrate the benzoylamido acid just described. When it was carried into fuming nitric acid at ordinary temperatures a violent reaction took place, the compound was completely broken up, a large amount of gases given off and the liquid heated. A variety of methods for moderating the reaction were tried. The following were reasonably successful.

I. Into a mixture of equal parts of concentrated nitric and acetic acids, cooled down to 0° C., small portions of the powdered compound were slowly carried. This would go on for a short time, the compound dissolving in the mixture, until suddenly the mixture would get red, the temperature rise considerably, and gases come off freely. The mixture had to be thrown, immediately at this point, into ice-cold water. If allowed to stand the temperature would continue to rise and the compound would be entirely destroyed, as in the first instance. It was impossible to stop the reaction exactly at the right point, even under these conditions. A considerable amount of picric acid was always found among the products. The nitro compound appeared in the cold water as a bulky, flocculent, yellow precipitate. The aggregate of nitro product by this method was so unsatisfactory that I sought a better method.

II. I obtained a much larger amount of the desired compound, though still far less than the calculated amount, when α-benzoylmetamidosalicylic acid was dissolved in 20 or 30 times its weight of acetic acid, four or five drops of nitric acid were added to each 100 cc. and the mixture warmed to about 80° C. As soon as the proper temperature was reached the liquid became suddenly a beautiful light yellow color. It was then immediately thrown into about four times its volume of water; otherwise a decomposition set in. Sometimes some unchanged amido acid appeared alongside of the nitro product.

The nitro compound crystallizes well out of alcohol and is easily purified. It is a handsome compound, crystallizing in glistening yellow plates. Heated up above 150° C. it gives off red vapors and then melts at 250° C.

It is easily soluble in strong acetic acid, somewhat less in alcohol, still less in benzol and naphtha, and very little soluble in water.

ANALYSES.—*Carbon and Hydrogen.*

0.2385 gram of this nitro compound separated from its well-crystallized barium salt, recrystallized out of the alcohol solution and thoroughly dried, gave 0.4522 gram CO_2, equal to 0.12332 gram carbon; and 0.0765 gram water, equal to 0.00850 gram hydrogen.

Nitrogen.—I. 0.3552 gram same compound gave 44 cc. of nitrogen at 14° C. and 735 mm., equal to 0.050041 gram nitrogen.

II. 0.1700 gram from another nitration, purified in the same way gave 20.2 cc. nitrogen at 15° C. and 734 mm., equal to 0.022836 gram nitrogen.

Calculated for $C_6H_2, OH, (NO_2)_2NHCOC_6H_5$.		Found.		
			I.	II.
$C_{13} = 156$	$= 51.49$ per ct.	51.70 per ct.	...	...
$H_9 = 9$	$= 2.97$ "	3.56 "	...	...
$O_6 = 96$	$= 31.68$ "	...	...	...
$N_3 = 42$	$= 13.86$ "	...	14.08 per ct.	13.42 per ct.

The compound first expected was a nitro-benzoylamidosalicylic acid. Calculated for this :

C_6H_2, OH, NO_2, $NHCOC_6H_5$, COOH.
$C_{14} = 168 = 55.62$ per cent.
$H_{10} = 10 = 3.31$ "
$N_2 = 28 = 9.27$ "
$O_6 = 96 = 31.80$ "

The nitro compound examined turns out to be a dinitrobenzoylamidophenol, instead of the mononitrocarboxylphenol which we look for. The —COOH group and one H atom have been driven out of the compound by the nitration and two —NO_2 groups have entered into it in their place. I failed to find anything in the various mother-liquors which were examined, except some benzoic acid and a little picric acid, which undoubtedly resulted from the decomposition of the compounds.

A large variety of methods were tried, without success, in the effort to find the conditions under which a mononitrocarboxyl acid would be formed. I always obtained, when there was any reaction at all, the dinitrophenol just described, and this alone. The great ease with which this reaction takes place renders it improbable that any other product can be obtained from *α*-benzoylmetamidosalicylic acid and nitric acid.

I may instance one attempt. Three or four drops of nitric acid were added to about 50 cc. of concentrated acetic acid, in which a little of the benzoylamido acid had been dissolved, and the open beaker was put under a bell-glass over caustic potash until the whole had dried up. Although the largest portion of the amido acid remained unchanged, some of the dinitrophenol was formed and nothing else.

The expulsion of the carboxyl group is a frequent occurrence under these circumstances. A number of cases where it has occurred in compounds similar to this could be cited. Hübner and Babcock[1] note it in the case of a compound closely allied to our benzoylmetamidosalicylic acid. By the nitration of β-metanitrosalicylic acid, β-dinitrophenol (melting point 63°–64° C.) was always produced alongside of dinitrosalicylic acid. In their case

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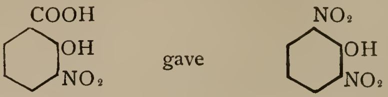
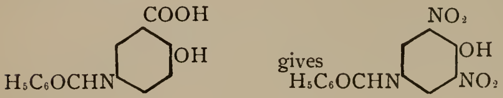
[1] Ber. d. deutsch. chem. Gesell. **12**, 1346.



In our case



The —OH group determines the location of the entering negative groups in both these cases, as usual, and in both products we find a carboxyl group replaced by a nitro group.

Salts.—Benzoylparamidodinitrophenol appears to be a fairly strong acid, and forms stable and, in the main, finely crystallizable salts. The solutions of its salts are all deep bluish red All of the salts have a rich gold-like lustre. The salts of the alkalies and alkaline earths crystallize especially well. Besides these described below, I have formed a zinc salt, which crystallizes in blunt, bright red needles, and is very soluble in water, and a silver salt, which crystallizes in wartlike masses made up of very small reddish-yellow needles, which are much less soluble.

The Potassium Salt, $C_6H_2(NO_2)_2$, $NHCOC_6H_5$, $OK . HO_2$. This salt was obtained by warming the phenol with a solution of pure potassium carbonate. The salt is very soluble in water. It is less soluble in dilute alcohol, and can be more readily crystallized from this. It forms handsome light red needles, with a splendid golden yellow lustre. The water-free salt is a dark brick-red color.

ANALYSIS.

Water.—0.5336 gram of the air-dried salt lost very slowly up to 180° C. 0.0280 gram water and then remained constant.

Calculated for $C_6H_2(NO_2)_2$, $NHCOC_6H_5$, $OK . H_2O$.	Found.
Water = 5.04 per cent.	5.24 per cent.

Potassium.—0.5056 gram of the water-free salt gave 0.1320 gram potassium sulphate, equal to 0.05924 gram potassium.

Calculated for $C_6H_2, (NO_2)_2, NHCOC_6H_5, OK$.	Found.
K = 11.46 per cent.	11.71 per cent.

The Barium Salt, $(C_6H_2, (NO_2)_2, NHCOC_6H_5; O)_2Ba . 3H_2O$. When the phenol is boiled with barium carbonate a deep bluish red solution is formed. This is filtered off and allowed to cool, when the fine, bright red needles of the barium salt usually appear at once. The salt is perfectly pure after being recrystallized twice. It has the same brilliant yellow lustre as the potassium salt, although not quite so bright. The water-free salt is a dark dead red.

ANALYSIS.

Water.—0.5336 gram of the air-dry salt lost at 210° C. all of its water, 0.0365 gram. The salt loses its water with difficulty.

Calculated for $C_6H_2, (NO_2)_2, NHCOC_6H_5, O)_2 Ba. 3H_2O$.	Found.
H_2O = 6.79 per cent.	6.82 per cent.

Barium.—I. 0.3256 gram of the water-free salt gave (the phenol precipitated and filtered off, and the barium determined in the filtrate), 0.1011 gram barium sulphate, equivalent to 0.059446 gram barium.

II. 0.1646 gram of the water-free salt gave (heated with H_2SO_4 until all of the organic matter was driven off), 0.0522 gram of barium sulphate, corresponding to 0.030693 gram barium.

Calculated for $(C_6H_2, (NO_2)_2, NHCOC_6H_5, O)_2 Ba$.	Found. I.	Found. II.
Ba = 18.49 per cent.	18.25 per cent.	18.64 per cent.

The Calcium Salt, $(C_6H_2,(NO_2)_2,NHCOC_6H_5, O)_2Ca. 4\frac{1}{2}H_2O$, was produced in similar manner to the barium salt. It crystallizes in glistening, yellowish-red scales or plates, which are quite soluble in water.

ANALYSIS.

Water.—0.4266 gram air-dry salt lost, at 200° C. heated, 0.0478 gram water, and remained constant.

Calculated for $(C_6H_2(NO_2)_2, NHCOC_6H_5, O)_2Ca.4\frac{1}{2}H_2O$.	Found.
H_2O = 11.17 per cent.	11.20 per cent.

Calcium.—0.3788 gram water-free salt gave 0.0840 gram calcium sulphate, corresponding to 0.02461 gram calcium.

Calculated for $(C_6H_2(NO_2)_2NHCOC_6H_5O)_2Ca$.	Found.
Ca = 6.20 per cent.	6.49 per cent.

The Lead Salt, $(C_6H_2(NO_2)_2NHCOC_6H_5, O)_2Pb$. Anhydric? This salt was precipitated when acetate of lead was added to a concentrated hot solution of the pure potassium salt. It forms a dark red crystalline mass, which dissolves in much warm water.

ANALYSIS.

Water.—Heated up to 180° C. it lost very little in weight, and did not change at all in appearance as did the other salts on heating.

Lead.—0.3520 gram dry salt gave 0.1290 gram lead sulphate, corresponding to 0.0886 gram lead.

Calculated for $(C_6H_2, (NO_2)_2, NHCOC_6H_5, O)_2Pb$.	Found.
$Pb = 25.49$ per cent.	25.17 per cent.

It follows from these analyses that this nitro compound obtained as described from α-benzoylamidosalicylic acid, has the general formula $C_{13}H_9N_3O_6$. We have already referred to the ground for believing that at least one NO_2 group has fastened upon the phenol group. The removal of the COOH group in the nitration renders this much very probable. But the other NO_2 group may be fastened upon the benzoyl group (—COC_6H_5) and the rational formula may be C_6H_2, OH, NO_2, $NHCOC_6H_4NO_2$. Such a compound is known. Güssefeld[1] has produced from other material the very phenol which might be expected here, and has established its constitution. By nitrating benzoylparamidophenol (the amido group in the same position as in our phenol) with concentrated nitric acid, he produced a dinitro compound with the same general formula as our phenol. By splitting off from this a well-known nitrobenzoic acid (C_6H_4, NO_2, COOH), he showed, however, that his compound was a nitrobenzoyl-paramidonitrophenol. That is, Güssefeld found that
C_6H_4, OH, $NHCOC_6H_5$ (para) (melting point 227.5° C.) gave C_6H_4, OH, NO_2, $NHCOC_6H_4$, NO_2.
While I claim that C_6H_3, OH, COOH, $NHCOC_6H_5$ (para) produces C_6H_2OH, NO_2, NO_2, $NHCOC_6H_5$.

A comparison of the properties of these compounds sustains the opinion that they are different bodies. The solubilities are entirely different. Güssefeld's compound is, for example, dissolved in alcohol only in traces, and is very difficultly soluble in concentrated acetic acid. His dinitro product melts at 225° C., my product at 250° C., etc. Sharper distinctions than these were hardly possible. The following investigations put this hypothesis about the constitution of the molecule of our dinitrophenol entirely beyond doubt:

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[1] Dissertat. Göttingen, 1880.

Decomposition of Benzoyl-paramidodinitrophenol with Hydrochloric Acid.

About one gram of the dinitrophenol was heated in a sealed tube with 5 cc. of concentrated hydrochloric acid and 3 cc. of water to 130° C. for about twelve hours. The phenol was completely dissolved. Upon cooling a bulky crystalline mass separated out.

Benzoic Acid.—The solid part was filtered off, washed with a little cold water, and recrystallized by dissolving in hot water and letting cool. The crystals continuing to have a yellow color, they were boiled with barium carbonate and the filtrate evaporated down closely. The little scales which crystallized out were yellowish at first, but after recrystallization they were entirely colorless. Small, glistening scales or plates, very soluble in water. The acid obtained from this salt crystallized in shining white, flat needles or plates, somewhat flexible. Melting point 118°—119° C. The unmistakable odor of benzoic acid. The acid was compared as to solubility, etc., with benzoic acid produced in the ordinary way. The melting point of benzoic acid is given in the books at 120° C., but none I could get melted higher than 119° C. The barium salts were compared also. There could be no doubt about this product being benzoic acid.

Diorthonitroparamidophenol or Isopicraminic Acid (melting point 170° C.)

The yellow filtrate was evaporated to dryness. The reddish brown crust which remained was washed with cold water and then dissolved in hot water. As the rather concentrated solution became cool, suddenly a lot of beautiful little needles separated out. Upon recrystallization, fine, long, thin crystals were obtained. In the liquid, and while still wet, they shone like gold. Dried in the air on porous paper the crystals lost this beautiful lustre and became a dead brownish yellow. This appeared to be due to the formation of just the thinnest film of some oxidation product over their surface. The large crystals, which appear to the naked eye to be individual needles, were resolved, under the microscope, into bundles of exceedingly fine, delicate little needles.

The compound dissolves very easily in alcohol; in benzol and naphtha less easily. It is very little soluble in cold water, but easily in hot. The finest crystals were obtained from the water solution. The solution in benzol yields yellowish-brown bundles of needles; in chloroform coarser dark brown needles, which approach nearer to plates in shape. All of these solutions are of a beautiful cherry-red color. Very dilute solutions have a delicate rose tint. Crystallized from these various solutions, the compound melted uniformly, after the fine large crystals had been once obtained, at 170° C. It appeared to decompose as it melted. Allowed to cool and heated a second time it always melted much lower.

The compound appeared to combine with strong acids, like hydrochloric, dissolving in them to form light yellow solutions. The acid probably unites with the amido group in the compounds, but the resulting compound could not be obtained separate from the liquid. The compound unites with alkalies to form well-crystallized, handsome salts, all of whose solutions have a fine, deep bluish red color, nearly the same tints, but much darker than the solutions of the free compound.

ANALYSIS.

Hydrogen and Carbon.—0.2832 gram of the compound, dried over H_2SO_4, was burned with oxide of copper and gave 0.3720 gram CO_2, corresponding to 0.10145 gram carbon and 0.0664 gram H_2O, corresponding to 0.007377 gram hydrogen.

Nitrogen.—0.1485 gram of the air-dry compound gave 27.7 cc. of nitrogen, measured at 24° C. and 749 mm., corresponding to 0.030608 gram nitrogen.

Calculated for $C_6H_2OH,(NO_2)_2,NH_2$.	Found.
$C = 36.13$ per cent.	35.82 per cent.
$H = 2.51$ "	2.60 "
$N = 21.10$ "	20.60 "

Salts.—The salts of the alkalies have been mentioned. I lost a good deal of material in trying to get salts of barium and calcium. They did not crystallize at all well, and I have not, so far, been able to get them sufficiently pure for analysis. This compound and its salts explode pretty sharply when strongly heated. This property, which it was difficult to avoid, caused me to lose several analyses. This explains how it is that I have no more analyses of the original compound and its salts to present at this time.

The Potassium Salt.—$C_6H_2(NO_2)_2NH_2OK$.

This was formed by bringing together the weighed amount of potassium carbonate and the phenol in warm water. The compound is a rather strong acid and attacks the carbonates in the cold. A beautiful bluish-red solution is at once formed. The salt is so very soluble in water that I could not get good crystals from this solution. It was evaporated to dryness and the residue dissolved in alcohol. The salt crystallizes from this solution in bluish-black needles.

Water?—The salt which had been dried over sulphuric acid was heated up to 130° C. without losing appreciably in weight.

Potassium determination.—After several vain attempts, a determination of potassium as the sulphate was obtained, as follows: The powdered salt was weighed out into a platinum crucible. A little concentrated sulphuric acid was added, and it was warmed very gently for a considerable time, until all of the salt was decomposed and the nitro compound had been quietly but completely broken up by the acid. It was then strongly heated and a perfectly pure sulphate obtained. 0.1948 gram of the salt dried at 130° C. gave 0.0760 gram of potassium sulphate, corresponding to 0.034124 gram potassium.

Calculated for $C_6H_2,(NO_2)_2,NH_2,OK$.	Found.
$K = 16.9$ per cent.	17.5 per cent.

From these analyses it is sufficiently evident that we have here a dinitroamidophenol or a compound with the picraminic acid formula. In agreement with our preconceived opinion, based upon a comparison of the last compound with Güssefeld's compound, it is now proved that both of the nitro groups went into the phenol. We get, by splitting, the well-known benzoic acid and a dinitro compound.

Picraminic acid was prepared in the usual way and compared carefully with the isopicraminic acid. Ordinary picraminic acid crystallizes from water in orange-red needles, which melt at 165° C. The solubilities are very different. 100 parts of water at 22° C.

were found to dissolve 0.140 part of picraminic acid and only 0.082 part of the new acid. Picraminic acid is very little more soluble in hot than in cold water, while 100 parts of hot water (just under boiling) dissolve 0.812 part of the new picraminic acid. The potassium salts were compared also. For details see the table.

If this is an isopicraminic acid, the compound from which it was obtained was simply a benzoyl-isopicraminic acid, and the comparison of this with the benzoyl derivative of the ordinary picraminic acid, which has been produced from various materials and studied by several chemists, yields us another strong argument for the proposition that this is a case of isomerism and not one of identity.

Stuckenberg[1] obtained, as we saw in the beginning, by nitrating benzoyl α-amidonitrophenol, a benzoylamidodinitrophenol. This he describes as crystallizing in greenish-yellow needles and as melting at 218–219° C. Haarhaus[2] obtained a compound of similar composition from picraminic acid itself, which he describes in like terms. Lastly, Stünkel[3] produced a dinitro-benzoylamidophenol by nitrating benzoylorthoamidophenol, from which he then procured the old picraminic acid in a way exactly parallel to the method in which I have prepared isopicraminic acid from my dinitro-benzoylamidophenol. He describes his dinitro product as crystallizing in greenish-yellow needles and having a melting point 220° C. My dinitrobenzoylamidophenol crystallizes in glistening yellow plates and melts, decomposing at the same time, at 250° C.

Through the courtesy of Dr. Stünkel in putting portions of his original preparations at my disposal, I was enabled to make myself a thorough comparison of these two benzoyl derivatives of the two isomeric acids and their salts. The differences are very marked all the way through. The salts of the longer-known phenol are all of a lighter yellow color and less lustrous than the salts of the new phenol. The latter are characterized by a more decided red color. The differences between the barium salts are otherwise quite distinct. The water of crystallization is different. The barium salt of the older phenol is very difficultly soluble in water, while the salt of the newer is easily soluble. Further details will be found in the table.

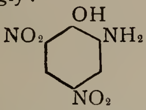
[1] *Loc. cit.*

[2] *Loc. cit.*

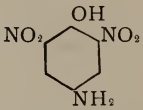
[3] *Loc. cit.*

The isomerism is readily explained when we consider the constitution of the material from which the isopicraminic acid was derived. The amido group in ordinary picraminic acid stands, as as we saw, in the ortho position. In the acid from which we started it stands, as we found, in the para position to hydroxyl (meta to carboxyl). If a transposition of the groups has not taken place then—and this is hardly conceivable in the case of a nitration taking place so very easily and at so slow a temperature as ours did—the resulting dinitroamidophenol must necessarily be isomeric and not identical with the known dinitroamidophenol or picraminic acid.

The graphical formulas of the two picraminic acids must be accordingly:



Orthoamidodinitrophenol
or Picraminic acid.



Paramidodinitrophenol
or Isopicraminic acid.

Comparison of Picraminic Acid, Isopicraminic Acid, and their Derivatives.

Picraminic Acid or Orthoamidodinitrophenol. — $C_6H_2OH(NO)_2NH_2$. Melting point 165° C. Crystallizes from water in orange-red needles, from chloroform in blood-red scales. Soluble in alcohol, little in water, hot or cold. Solutions an orange-red color.[1]	*Isopicraminic Acid or Paramidodinitrophenol.* — C_6H_2OH, $(NO_2)_2NH_2$. Melting point 170° C. Crystallizes from water in bundles of exceedingly fine needles, having a golden lustre when wet, brownish yellow when dry. Very easily soluble in alcohol, easily soluble in warm water, very little in cold. Solutions bluish red.
Potassium Salt.—$C_6H_2(NO_2)_2NH_2OK$. Red, translucent rhombish plates, which are rather soluble in water, but little soluble in alcohol. Explodes on heating strongly.[1]	*Potassium Salt.*—$C_6H_2(NO_2)_2NH_2OK$. Bluish-black needles. Extremely soluble in water, less in alcohol. Explodes sharply when strongly heated.

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[1] Girard, Jour. für pract. Chem. **59**, 142, and Compt. rend. **36**, 421.

Benzoylorthoamidodinitrophenol, or Benzoylpicraminic Acid. $C_6H_2OH, (NO_2)_2NHCOC_6H_5$ (ortho). Melting point 220° C.[1] Greenish-yellow needles, difficultly soluble in warm concentrated acetic acid, still more difficultly in alcohol and benzol, almost completely insoluble in water (Stünkel).

Potassium Benzoylpicraminate.—$C_6H_2(NO_2)_2$, $NHCOC_6H_5$ (ortho), OK, $2H_2O$.[1] Small beautiful reddish-yellow needles, which dissolve easily in water and dilute alcohol. Water-free, very dark red (Stünkel).

Barium Benzoylpicraminate. $(C_6H_2(NO_2)_2, NHCOC_6H_5, O)_2$ Ba. $5H_2O$.[1] Shellac-red needles. Dissolves in water with extreme difficulty (Stünkel).

Benzoylparamidodinitrophenol, or Benzoylisopicraminic Acid. $C_6H_5OH, (NO_2)_2NHCOC_6H_5$ (para). Reddish plates, having a splendid golden lustre. Quite soluble in alcohol and acetic acid, very little soluble in benzol and water. Melting point 250° C. decomposing.

Potassium Benzoylisopicraminate.—$C_6H_2(NO_2)_2NHCOC_6H_3$ (para) OK, H_2O. Fine red needles with a splendid golden lustre. Very easily soluble in water, somewhat less in alcohol. Water-free, brick-red.

Barium Benzoylisopicraminate.—$(C_6H_2(NO_2)_2, NHCOC_6H_5, O)_2$ Ba. $3H_2O$. Fine delicate red needles with a golden lustre. Dissolves in warm water easily; in cold, less easily. Water-free, dark red.

The larger part of this work was done in the chemical laboratory of the University of Göttingen, during 1879 and 1880, and I am indebted to Prof. H. Hübner for invaluable advice in connection with the investigations. I purpose further perfecting the determinations here reported, and pursuing the several lines of investigation which have been started, as rapidly as the spare time can be ound.

LABORATORY OF THE N. C. AGRICULTURAL EXPERIMENT STATION, RALEIGH, *Dec.* 1882.

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[1] Stünkel, Dissertat. Göttingen, 1880, 18.

PISCIDIA, THE ACTIVE PRINCIPLE OF JAMAICA DOGWOOD (*Piscidia Erythrina*).

By Edward Hart.

The fluid extract of Jamaica Dogwood, obtained from the bark of the root, has been introduced to the notice of the medical profession by Parke, Davis & Co., of Detroit, Mich., to whose kindness I owe a supply of material for this investigation. It is "stated by medical men to be a direct sedative, producing narcotic effects which are refreshing, and not followed, like opium, by hyperaemia of the brain, nausea and general nervous disturbance. It is said to be of value in bronchitis, asthma, nervous cough, writer's cramp, spasms of muscles due to functional causes, chorea, tetanus, and especially in toothache to relieve pain."[1] The physiological action of the extract[1] and also of the active principle[2] has been studied by Dr. Isaac Ott, of Easton. After many fruitless trials I succeeded in separating the active principle as follows: The contents of a pound bottle were poured into a flask in which 30 grams of quicklime had been slacked with enough water to form a thick paste. The lime was intimately mixed with the extract by shaking, allowed to stand in a warm place for half an hour, filtered and the residue pressed. Water was then added until the solution became slightly turbid. After standing two or three days, crystals of piscidia separate on the sides and bottom of the flask, accompanied with more or less resinous substance, from which they can be easily separated by recrystallization from alcohol. By adding water to the liquid poured off from the crystals of impure piscidia, a second crop of the crystals still more impure can be separated. I have succeeded in obtaining about ½ gram piscidia from each bottle of extract, which corresponds to 1 pound of the root bark. The resinous substance which separates on adding a large quantity of water to the filtrate from the piscidia crystals still contains piscidia in small quantity, but I doubt whether the total amount contained in each bottle can be much over a gram.

Piscidia, $C_{29}H_{24}O_8$.

The active principle after many recrystallizations from alcohol is obtained in the form of small, nearly colorless crystals, which appear under the microscope to consist of four or six-sided prisms.

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[1] Ott. Detroit Lancet, June, 1880.

[2] Archives of Medicine, Feb. 1881.

It melts at 192° (uncorrected). Piscidia is insoluble in water, slightly soluble in cold, much more in boiling alcohol, only slightly soluble in ether, easily soluble in benzene and chloroform. It dissolves in strong hydrochloric acid, and is reprecipitated, apparently unchanged, by dilution with water. It dissolves in cold concentrated sulphuric acid and separates again by addition of water, but this treatment appears to change its properties, as it no longer dissolves easily in alcohol. Boiling with dilute and strong acid causes no separation of sugar. An alcoholic solution of lead acetate gives no precipitate. The alcoholic solution is neutral to litmus paper. The analysis resulted as follows:

(1) .1780 gram gave .4555 gram CO_2 and .0939 $H_2O = 69.78$ per cent. C and 5.86 per cent. H.

(2) .2323 gram gave .5942 gram CO_2 and .1077 $H_2O = 69.76$ per cent. C and 5.15 per cent. H.

(3) .1473 gram gave .3765 gram CO_2 and .0714 $H_2O = 69.69$ per cent. C and 5.38 per cent. H.

These combustions were made in a stream of oxygen. On examination the oxygen used was found to contain hydrogen,[1] no doubt derived from having been kept in a metallic (galvanized iron) gas-holder. It is well known that oxygen made from potassium chlorate contains a small quantity of chlorine. Another combustion was then made, the oxygen being passed through a red hot platinum tube before entering the apparatus used in drying the gas and freeing it from CO_2. Only the water was determined.

(4) .3660 gram gave .1642 gram $HO_2 = 4.98$ per cent. H.

	Calculated.		Found.			
			(1)	(2)	(3)	(4)
C_{29}	348	69.60	69.78	69.76	69.69	
H_{24}	24	4.80	...	...	...	4.98
O_3	128	25.60				
	500	100.00				

As far as could be ascertained the fluid extract owes its poisonous properties entirely to the piscidia it contains, at least the filtrate from the lime contains apparently no other substance except the resinous substance already mentioned. This appears to contain a little piscidia which cannot be entirely separated from it. I have not examined the lime precipitate.

LAFAYETTE COLLEGE, *Feb.* 1883.

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[1] Compare Lieben, Annalen der Chem. **187**, 142.

Communications from the Chemical Laboratory of Rutgers College.

IX.—ESTIMATION OF CHLORINE, SULPHURIC ACID, AND CHROMIUM IN THE PRESENCE OF ORGANIC MATTER.[1]

By Charles T. Pomeroy.

The determination of chlorine, sulphuric acid, and chromium in the presence of organic matter, as in the case of the analysis of many dye-stuffs, is a matter of considerable difficulty. It is necessary to get rid of the organic matter by ignition with alkali carbonate and nitrate, else the determination of the chromium will not be reliable. During the oxidation of the organic matter a portion of the nitrate is reduced to nitrite, and on acidifying the solution, preparatory to the precipitation of the chlorine, the nitrous acid reduces some of the chromate to green chromous chloride, in the presence of which silver nitrate fails to precipitate the whole of the chlorine.[2] If an attempt is made to precipitate the sulphuric acid in this solution, it will be found that the barium sulphate retains chromic oxide.[3]

It becomes necessary, therefore, after destruction of the organic matter, to entirely convert the chromium into a chromic salt before the chlorine and sulphuric acid can be determined with accuracy. The reduction with alcohol is not practical in this case, since chlorhydric acid must be added. Neither can the reduction by means of hydrogen sulphide be taken advantage of; for, on standing in a warm place, there is danger, not only of losing chlorhydric acid, but also of oxidizing a portion of the hydrogen sulphide to sulphuric acid. The reduction with sulphurous acid is out of the question, for similar reasons.

The following method I have found to give satisfaction. To the solution of chromate containing sulphates, chlorides, chromates and salts of chromium, obtained by extraction of the mass which has been fused with alkali carbonate and nitrate, and filtration from the residue, which contains the iron, lime and magnesia, a solution of potassium, sodium, or ammonium nitrate is added and then nitric acid in excess. After standing in the cold for about twelve hours, ammonium hydroxide is added and the whole boiled, the precipitate of chromic hydroxide filtered off, washed with hot water (best with the aid of a filter pump) and estimated as usual. In the filtrate from the chromic hydroxide, the sulphuric acid is estimated as barium sulphate, by precipitation with barium nitrate and nitric acid. It is occasionally necessary to purify the barium sulphate by fusion with sodium carbonate and reprecipitation.

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[1] This research was begun in the College Laboratory and finished in Mr. Pomeroy's private laboratory in Newark.—P. T. Austen.

[2] Peligot. Fres. Quant. Anal., Last Am. Ed. 432.

[3] Fres. Quant. Anal. 1876, 354.

In the filtrate from the barium sulphate, the chlorine is precipitated by silver nitrate as usual.

In the presence of an alkali nitrite and nitric acid, the reduction of the chromic acid takes place immediately on boiling the solution. Advantage may be taken of this when it is required to determine the sulphuric acid alone, since in this case there is no danger of loss on boiling.

The chromates are reduced to chromic salts by the nitrite, which passes into nitrate, while the chromous salts are oxidized by the nitric acid into the chromic state.

The following analyses were made to test the accuracy of the method:

10 cc. of a dilute chlorhydric acid gave

	I.	II.	Mean.
AgCl	1.0794	1.0790	1.0792

Dissolved 2.4 grams or $K_2Cr_2O_7$ in 200 cc. water:

	I.	II.	III.[1]	Mean.	Calc.
25 cc. $K_2Cr_2O_7$ solution	.3000 gram	.3000 gram	.3000 gram	.3000 gram	...
	5 cc. HCl	5 cc. HCl	5 cc. HCl	5 cc. HCl	...
Cr_2O_3 found	.1561	.1559	.1550	.15566	.15543
AgCl "	.5397	.5399	.5391	.53956	.5396

In these analyses the acid was neutralized with ammonium hydroxide, sodium nitrite and then nitric acid added. It was not thought necessary to check the sulphuric acid determinations, as there was nothing in the method to interfere with this determination. In practice, the duplicate results agreed excellently.

In the analysis of commercial chrome-yellow by this method, the lead, even when present as sulphate and chloride, passes entirely into solution upon adding sodium nitrite and nitric acid in sufficient quantities and boiling.

[1] Nos. 1 and 2 were precipitated in glass, No. 3 in porcelain.

Sodium nitrite suitable for this purpose can be prepared by simply heating to redness for some time in a closed iron vessel, sodium nitrate, free from sulphates, chlorides, and silica, until nearly one molecule of oxygen has been driven off, and then dissolving the mass in water and filtering off the oxide of iron and other insoluble impurities.

The crude sodium nitrate can be purified by dissolving the commercial article in water, filtering, precipitating sulphuric acid, if it contains any, with barium nitrate, filtering, precipitating the barium with sodium carbonate, filtering, adding an excess of nitric acid, and heating with small additions of nitric acid, until free from chlorine, nearly neutralizing with sodium carbonate and then crystallizing.

The method of preparing sodium nitrite mentioned by Fresenius[1] has not proved satisfactory in my hands, as the one just given. In almost all cases the bottom of the iron vessel melts out. In one case, the iron bottom, which was a quarter of an inch thick, melted out within fifteen minutes at a hardly visible red heat. The product thus obtained is also very liable to contain but little nitrite, being almost all transformed into the hydroxide, and hence has but little reducing effect on the chromates. It is perhaps possible that the oxide of lead acts as a carrier of oxygen to the iron, taking up oxygen from the nitrate and giving it up to the iron. In this way a small quantity of lead oxide might effect the destruction of a large amount of iron.

New Brunswick, N. J.

Contributions from the Chemical Laboratory of Harvard College.

XXX.—A MODIFICATION OF NOACK'S METHOD FOR PREPARING CARBONIC OXIDE.

By Leonard P. Kinnicutt.

In the Berlin Berichte, volume 16, page 75, E. Noack shows that carbonic oxide can be obtained by passing carbon dioxide over zinc dust. The idea that the same gas might be more conveniently made by heating carbonates directly with zinc dust, led me to try a series of experiments with magnesite. I found that when powdered magnesite mixed with twice its weight of zinc dust, is placed in a copper retort and heated so that the bottom of the retort is nearly surrounded by the flame, a gas is immediately given off, which, after the first five minutes, is nearly pure carbonic oxide. For the first five minutes, the gas is a mixture of carbonic oxide, carbon dioxide, and in case the substances were not perfectly dry, a little hydrogen. In place of a retort, hard combustion tubing can be used.

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[1] Qual. Anal., Last. Am. Ed. 71.

An analysis of the gas, when given off at the rate of about four bubbles a second, collected directly from the retort and measured over mercury, gave the following result:

Volume of gas 152.5. $P = 583.4$. $t = 4°$. Cor. $V = 115.4$.

After absorption of CO_2 by KOH: Volume of gas 150.0. $P = 588.8$. $t = 5°$. Cor. $V = 114.7$.

Per cent. $CO_2 = 00.61$.

I have undertaken the study of the decomposition of other carbonates, but as a method for preparing carbonic oxide the above is in every way satisfactory; the manner in which the gas is given off resembling that of oxygen when made from potassium chlorate, with the advantage that the evolution is more easily controlled.

March 17, 1883.

METHODS OF ANALYSING SAMARSKITE

And the other Columbates containing Earthy Oxides, by the Agency of Fluorhydric Acid; and of Dissolving Columbite and Tantalite by the same Acid.—On the Separation of Thoria from the other Oxides.—Quantitative Estimation of Didymium Oxide in its Mixtures with other Earthy Oxides.

By J. Lawrence Smith, *Louisville, Ky.*

The study of this class of minerals has always presented considerable interest to the analytical chemist, from the time of the discovery of columbite by Hatchett in 1801, and tantalite and yttrotantalite by Ekeberg about one year later. These minerals for more than twenty years were the only known columbites and tantalites; since then about fourteen other well-defined species have been discovered and described, although the chemical formulæ of most of them are yet in doubt.

The metallic acids in these minerals have many interesting characteristics, which have already attracted special attention since H. Rose's researches in 1846 defining the distinctive characteristics of columbic and tantalic acid, which, prior to that date, had been considered by most chemists as being one and the same acid. M. Hermann, and later, M. Marignac, took up M. Rose's investigations and gave to them considerable extension. The former thinks that he has discovered two additional metallic acids of the same type in the minerals in which the first two are found. The metals of these acids he has called ilminium and neptunium.[1] The labors of M. Marignac, as set forth in his various publications,[2] have contributed very largely to our precise knowledge of certain very important compounds of these acids, and he has also given the only reliable method of a close quantitative separation of columbic and tantalic acid.

An interesting chemical characteristic of these minerals is, that nearly all of them have, as a portion of their bases, some one or more of the rarer earths, as the oxides of yttrium, erbium, cerium, thorium; and some new earths not yet fully defined. One reason for the comparatively imperfect study of the compounds of tantalum and columbium is the rarity of the minerals containing them; but since the discovery of comparatively large quantities of columbite and samarskite in the United States, this difficulty is removed. Another obstacle to their study arises from the method of decomposing them, this being attended with more or less inconvenience when large quantities are to be operated on. This last difficulty will, however, be removed to a considerable extent by the analytical facts to be detailed in this communication.

In my published investigations in connection with the columbic and tantalic acid minerals from new localities in the United States[3] (more especially the remarkable developments of samarskite in North Carolina), the object in view was to detail all that was connected with their mineralogy, to describe the new species I had discovered, and to give a clear idea of their constitution in comparison with the same minerals as found elsewhere. In the analyses in that paper I did not give the relative proportions of columbic and tantalic acids, assigning as my reason at the time for this omission that the method I had worked with (Rose's) proved too unsatisfactory to warrant the waste of time in seeking after results that I was satisfied would be inaccurate. In this view I was sustained by M. Marignac, who has devised a much better method, which I have since tried, and which gives very good approximate results, within 1½ to 3 per cent., according to the amount of tantalic acid present. In the same paper I stated that the earths in samarskite did not appear to contain cerium oxide as does the Ural variety of the same mineral, although in the analyses then given I preferred noting the earths of that group as cerium oxides[1] until I could arrive at more satisfactory conclusions by renewed researches; for it is known that a small quantity of cerium oxide mixed with other oxides of that group may escape detection when the entire amount of oxides treated is very small; so it was thought better to repeat the experiments on larger quantities before making any conclusive statement as to the presence or absence of cerium oxide. Thoria, also, if present in the North Carolina samarskite, was there in too minute a quantity to warrant me in pronouncing upon it by the usual method of separation. All doubt, however, on this head has been dispelled by an easy and certain method I have discovered of separating it from the other earths, and, although present in the proportion of less than 1 per cent. of the mineral, it can be separated and identified as well as any other constituent of the mineral, and that by operating with not more than three or four grams of the mineral.

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[1] Jour. für prakt. Chem. **15**, 105 Chemists are not ready to recognize these as new substances, but rather as mixtures of tantalic and columbic acids.

[2] Annales de Chim. et de Phys. **8**, 1866, 115–75.

[3] American Journal of Science, May, 1877, 360.

Method of Decomposing and Analysing Samarskite.

I shall first detail the method pursued in the analyses of samarskite, as this being one of the most complex of the columbates, all that is said in regard to it will be applicable to other forms of this class of natural compounds. The method most commonly employed for decomposing this mineral is by means of potassium bisulphate in the proportion of one part of mineral to six of potassium salt. This, it will be seen, introduces a very large amount of solid matter into the process, and besides, requires careful heating to redness for some time. A more recent and better method is that proposed by Prof. Wolcott Gibbs,[1] viz. by the acid potassium fluoride ($FlKFlHO$). This method was used by M. Marignac in his most admirable and exhaustive labors on tantalic and columbic acid compounds already referred to. Concentrated sulphuric acid when heated with some of the columbates will decompose them more or less, but cannot be used in their analysis. The method about to be described is a decided improvement on either of the above, for reasons that will be rendered very apparent.

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[1] By this group is meant all the oxides forming insoluble double salts with the potash and soda sulphates, amounting to about 4 per cent. of the mineral. Thoria, if present, was to be sought for among the oxides.

Decomposition by Fluorhydric Acid.[2]

The quantity of samarskite used in the analyses is usually five grams, and having an abundance of the material, special portions are used for the verification of certain results. The precipitates of all of the ingredients are so dense and granular that filters 7 to 10 cm. in diameter are used except in the iron precipitate. The mineral is triturated to a fine powder, and five grams, dried at 150° C.,[3] weighed and placed in a small platinum capsule; one of 50 cc. capacity is sufficiently large. This is moistened with about 5 or 6 cc. of water, and then from 8 to 10 cc. of concentrated fluorhydric acid is added (one-half at a time with an interval of two or three minutes), and the mixture stirred with a platinum rod. In a few seconds a vigorous action takes place; the mass becomes heated, and in from five to ten minutes the decomposition is complete without the application of heat. If the powder be exceedingly fine the decomposition is almost as rapid as that of calc-spar when chlorhydric acid is poured upon it.

The action is known to be complete by the disappearance of every black particle in the mass. The capsule is now placed on the water-bath to ensure complete decomposition and to evaporate away the larger portion of the liquid.

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[1] American Journal of Science, **37**, 355.

[2] Not many years ago this acid was made and used in comparatively small quantities, but owing to the extended use of it in the arts, it is now manufactured on a large scale. One of the largest manufacturers of this acid in this country is Feuchwanger, 118 Dey Street, New York, who furnishes a *fuming acid*, remarkably pure for a commercial article, at 25 cents per pound, in lead jugs of 30 lbs. capacity. The saturating property of 10 grams of this acid is equal to that of 23 grams of nitric acid of 1.42, costing 12 to 14 cents by the carboy, making the fluorhydric acid actually cheaper than the nitric acid. I have found in many laboratories what purports to be fluorhydric acid that is little less than sour water. When I desire pure fluorhydric acid, I distil the commercial acid of Feuchwanger in a small platinum still and condense in a very little distilled water, the vessel being surrounded by ice. In this way there is no annoyance from fluorsilicic acid.

[3] Avoid heating to redness, for by so doing the mineral is not so readily acted on by the fluorhydric acid. I determine the loss by heat on a separate portion of one gram.

After the reaction the contents of the capsule are, 1st, a clear colorless solution; and 2d, a heavy green precipitate. The *solution* contains all the metallic acids, oxides of iron and manganese. The *insoluble portion* contains all the earths and uranium oxide. It is true that traces of iron will be subsequently found in the analysis of the insoluble part and traces of earth in the solution, but they are easily separated in the course of the analysis and properly placed in the estimates. They, however, only represent a fraction of one per cent.

It will be seen that thus far in a very few minutes the samarskite has not only been decomposed but partly analyzed, for this perfect separation into two parts facilitates to a vast extent the subsequent operations.

To the contents of the capsule, decomposed as above stated, 30 cc. of water are added, the whole is then warmed and thrown on a filter (8 cm.) in a gutta-percha or silver funnel, the filtrate being received in a platinum capsule. The filtration takes place very rapidly and the precipitate is well washed with hot water, a few drops of fluorhydric acid being added towards the end of the washing, to prevent a trace of the precipitate passing through the filter, which might otherwise occur. The filtering and washing is accomplished in fifteen or twenty minutes. As already stated we have two classes of substances completely separated from each other, one soluble, the other insoluble. The soluble we call A, the insoluble we call B.

We will first consider A. This solution is evaporated over a water-bath, and before it reaches dryness, concentrated sulphuric acid is added in excess to decompose the fluorides, about 1 cc. acid to every gram of metallic acid supposed to be present. The evaporation is completed by careful heating over the flame until the decomposition is complete and nearly all the sulphuric acid has been driven off. After cooling, water is added acidulated with chlorhydric acid, the contents of the capsule washed out into a glass flask capable of holding one litre. When 5 grams of the mineral have been used the liquid mass should be half a litre. A little chlorhydric acid is added. This is now boiled for one or two hours,[1] which can be done in an ordinary bottle.

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[1] In my laboratory the boiling of liquids containing a heavy precipitate is always accomplished by driving steam through from a glass flask or small boiler, with two tubes, one bent at two right angles to drop in the liquid, and the other a straight one for a safety tube, thus preventing all thumping.

After boiling, the contents of the vessel are thrown on a filter and thoroughly washed with hot water. The insoluble part remaining in the filter is columbic and tantalic acids with a little tungstic and stannic acid. This is dried, ignited and weighed with all the usual precautions, and afterwards the tungstic and stannic acids are separated in the manner described by Rose, and the columbic and tantalic acids by Marignac's method.[1]

The filtrate from the metallic acids is concentrated, and as it contains only iron and manganese, with mere traces of other oxides, they are separated and estimated in the usual way by the sodium acetate method. This disposes of part A.

We now pass to the portion B, which is the insoluble part remaining after the first treatment with fluorhydric acid, and is composed of the fluorides of the earths and uranium. It is washed from the filter into a small platinum capsule. To this sufficient concentrated sulphuric acid is added to decompose the fluorides (about 2½ grams suffice where 5 grams of minerals are used), and the whole is concentrated as far as possible over a water-bath, and carefully heated over the flame until the excess of sulphuric acid is driven off, or very nearly so. After cooling, about 50 cc. of water are added and the capsule is gently heated on a water-bath, when the mass dissolves completely, furnishing a bright green solution. A minute amount of insoluble matter may sometimes show itself; this belongs to the metallic acid, and is separated and added to that obtained from A. It is usually only a few milligrams. The green solution is heated over the flame and a little nitric acid is added, when the color is changed to a lemon yellow, from the higher oxidation of the uranium oxide. The solution is now introduced into a beaker and increased to about 250 cc. by the addition of water, and made to boil. It is then very nearly neutralized by ammonia, and oxalic acid or ammonium oxalate added very gradually. The precipitate, as is well known, will be first taken up and afterward become permanent. It consists of all the earths present. This is allowed to stand some 6 or 8 hours, then thrown on a filter and well washed. This oxalate of the earths I will call C, and proceed to treat of it a little further on. The filtrate contains all the uranium in solution with a trace of iron. This is concentrated to about 80 or 100 cc., and then a concentrated solution of ammonium carbonate is added, which first precipitates the uranium oxide and then redissolves it. The solution is nearly clear with the exception of a few flocci of ferric oxide. This is warmed gently and a few drops of ammonium sulphide are added, which precipitates every trace of iron. That is washed and estimated in the usual way, and represents from two- to three-tenths of one per cent. of the mineral, and is added to the ferric oxide obtained from solution A. The filtrate containing the uranium oxide is evaporated to dryness, the ammonium salts driven off, and the oxide estimated by the ordinary method. In all the analyses thus far no solid matter is introduced by the reagents.

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[1] Annales de Chim. et Physique, 8, 1866, 115–175.

Before quitting this part of the subject I would state that there is no columbate that does not readily yield to this treatment by fluorhydric acid, as euximite, hatchettolite, fergusonite, etc., and so completely separate these minerals into two classes of substances (the metallic acids in a state of solution and the earths as insoluble compounds) that the weighing of the acid decomposed by the action of sulphuric acid as described will give at once an idea of the quantitative composition of the minerals.

Columbite and Tantalite.

It is well to make some remarks in reference to the columbite and tantalite and their decomposition by fluorhydric acid, for they are more difficult to decompose by any method than are the columbites of the earths.

Before we had the more powerful and convenient methods of decomposing minerals, Berzelius, Rose and others had to resort to the finest possible subdivision of the mineral, often using a flat slab of agate and triturating with water. This fine trituration is sometimes, even now, employed in our present modes of manipulation. As the method I have adopted for years is more convenient than any I know of in use, it will not be out of place to refer to it here, for the whole operation is conducted in the same mortar in which the crushed mineral is first powdered.

If we have columbite to decompose, exceedingly fine dry trituration in an agate mortar suffices. To triturate properly, one gram of columbite will require from ten to fifteen minutes in a four-inch mortar. Thus pulverized, place the mineral in a platinum crucible or capsule, and add about five grams of fluorhydric acid of the strength alluded to in the first part of the paper; then heat over the flame on a plate of iron, so as to bring the temperature up to from 60 to 90 C. A half an hour suffices for complete solution; if any black powder remains, it is well to add a little more acid and heat again. A few flocci will sometimes appear in the solution, which is stannic oxide. In the analysis of tantalite the solution is not so easily accomplished, but I overcome that completely by my modification of the trituration of the mineral. After rubbing it up in the mortar for about five or six minutes I add a little strong commercial (95 per cent.) or absolute alcohol to the contents of the mortar, enough to cover completely the powder, then continue the trituration. The alcohol will soon evaporate; add a fresh portion; this I may have to repeat several times. The alcohol, like any other liquid, enables the pestle to reach thoroughly the coarser particles that always settle to the bottom. To triturate thoroughly, one gram of the tantalite requires about twenty minutes. The contents of the mortar are like imperfectly dried mud, and are kept at a temperature of about 150° C. in an air-bath for ten or fifteen minutes. A gram of the material is then placed in a capsule or crucible of platinum, thoroughly dried and carefully weighed. About five grams of the fluorhydric acid are now added, and the heating conducted as in the case of columbite. A half-hour suffices to complete the solution, which is a clear liquid with a few white flocci in it that I have proved to be stannic oxide. While this method of solution appears to be a little tedious, I can assure those who try it, that the manipulations are very simple, and there is no soluble matter introduced, as is the case when six or eight times its weight of potassium bisulphate is used. We now evaporate the solution of either columbite or tantalite to dryness, proceed as in the case of the samarskite. As there are no earths, however, in these minerals, there is little else than iron and manganese to deal with as associated with the metallic acids, which are decomposed by sulphuric for separation from iron and manganese as already indicated.

In regard to the separation of the two acids when they are in the same mineral, I use the method already referred to and first used by Marignac.[1]

The tungstic acid, stannic acid, etc., I estimate in the manner pointed out by Rose in his Analytical Chemistry.

(*To be continued.*)

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[1] Annales de Chimie et de Physique, 8, 60; 1866.

REVIEWS AND REPORTS.

On the Present Condition of the Soda Industry.[1]

From information kindly supplied to me by manufacturers in all the countries in which the soda industry is practised, I have been enabled to draw up a statement of the present total soda production of the world, and of the proportions in which that production is divided between the Leblanc process and the ammonia process. In drawing up the following table I have converted all the figures supplied to me, alike those for soda ash, those for crystals, those for caustic soda, those for bicarbonate, and those for black ash sold as such, into terms of pure Na_2CO_3:

Present Soda Production of the World.

	Leblanc Soda.	Ammonia Soda.	Totals.	Ammonia Soda per cent. of Total Soda.
Great Britain . .	380,000	52,000	432,000	12.0
France	70,000	57,125	127,125	44.9
Germany . . .	56,500	44,000	100,500	43.8
Austria	39,000	1,000	40,000	2.5
Belgium . . .	...	8,000	8,000	100.0
United States . .	...	1,100	1,100	100.0
Total . .	545,500	163,225	708,725	23.0

This table shows that the total quantity of soda now being manufactured annually is nearly 710,000 tons, and that of this quantity more than 163,000 tons are produced by the ammonia process.

Although it is now more than 47 years since the ammonia process was first proposed by Dyer and Hemming, it is less than 17 years since that process was first realized industrially. As an industrial process, capable of being worked continuously and with satisfactory commercial results, the ammonia process dates only from 1866, being the year in which M. Ernest Solvay, of Brussels, began to produce ammonia soda at works which he had established for the purpose at Couillet, near Charleroi. M. Solvay has now two other ammonia soda works in operation—one in France, at Varangeville-Dombasle, near Nancy, and one in South Germany, at Wyhlen, in the Grand Duchy of Baden—and by his courtesy I am enabled to place before you the following statement of the quantities of ammonia soda which he has manufactured in each complete twelve months from the first of May, 1866:

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[1] Abstract of a paper read by Walter Weldon before the Society of Chemical Industry, and published in the Journal of the Society.

	Tons.	
1866-67	179	Couillet only.
1867-68	465	
1868-69	719	
1869-70	940	
1870-71	1,862	
1871-72	2,805	
1872-73	3,423	
1873-74	3,980	
1874-75	4,678	
1875-76	5,768	Couillet and Dombasle.
1876-77	11,579	
1877-78	19,247	
1878-79	25,023	
1879-80	32,326	
1880-81	42,669	Couillet, Dombasle, and Wyhlen.
1881-82	53,400	

The competition of the ammonia process with the Leblanc process has thus attained its present degree of seriousness only very recently indeed.

While face to face with so serious an amount of competition, actual and imminent, on the part of the ammonia process, the Leblanc process pure and simple is now further threatened with what is surely the "most unkindest cut of all," namely, with competition from the Leblanc process itself—combined with the extraction of copper from Spanish pyrites.

To explain how this has come about I must remind you that the sulphuric acid used in the Leblanc process is now invariably manufactured from the sulphur of pyrites; that the pyrites used in this country is now almost exclusively either Spanish or Portuguese pyrites, containing two or three per cent. of copper and very small quantities of silver and gold; that after most of the sulphur has been burnt off from the pyrites, as the first step in the manufacture of sulphuric acid, the residual "burnt ore," or "pyrites cinders," as it is called, is treated by the wet way for the extraction from it of copper, and in most cases now of gold and silver also;[1] and that what remains when these have been extracted is an almost pure oxide of iron, which finds a ready sale for use for various purposes in connection with the manufacture of iron and steel. The supply of this cupreous pyrites is for the most part monopolized by three great companies—the Tharsis Company, the Rio Tinto Company, and Messrs. Mason and Barry. These companies not only supply nearly the whole of the pyrites used in the manufacture of sulphuric acid in England, but the Rio Tinto Company also supplies annually some 60,000 tons of pyrites to Germany, and is also beginning to send pyrites into Austria. None of the three companies, however, has been able to sell an ounce of pyrites in France.

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[1] A German analysis of Rio Tinto pyrites gives the following results per 1000 kilos:
495 kilos. Sulphur.
430 kilos. Iron.
30 kilos. Copper.
10 kilos. Lead.
26 grams Silver.
180 milligrams Gold.
150 grams Bismuth.

The course, then, which the Rio Tinto Company is taking is this. Unable to sell its pyrites to the French Leblanc soda-makers, it has determined that the Leblanc soda made in France, or at least a large part of it, shall nevertheless be made by means of Rio Tinto pyrites, and to this end it has promoted a subsidiary company, "La Compagnie d'Exploitation des Minerais de Rio Tinto," which company is to make Leblanc soda in France and elsewhere, relying for its profits neither on soda nor on chlorine, but on copper and oxide of iron. For this company soda and chlorine will be simply by-products, which it will be glad to sell at a profit, if that may be, but which, if that may not be, it will be content to sell at the bare cost of manufacturing them. It will manufacture them only for the sake of converting Rio Tinto pyrites into pyrites cinders.

This new company proposes to operate upon an enormous scale. It has a capital of £1,200,000 sterling, of which one-half is already paid up, and there is talk of its building in France no fewer than five great works: one of which, designed and to be managed by Englishmen, it has already commenced, in the neighborhood of Marseilles. The result cannot but be grave for the existing French Leblanc soda-makers, and must inevitably affect the makers, both of Leblanc soda and of ammonia soda, in this country also.

Moreover, this new company will not confine its operations to France. Not only will it take Spanish pyrites to the United States and there make sulphuric acid, extract copper, and obtain "purple ore,"—large quantities of which at present go from England to America,—but it will also build a large soda-making and copper-extracting works—which will certainly affect the English alkali trade—in the neighborhood of Antwerp. The Leblanc process will thus be reintroduced into Belgium, not as a substantive process, but simply as a part of a combination of processes for the utilization of cupreous pyrites.

To such complexion has the Leblanc process come at last. Originally, soda was its only commercial product, the hydrochloric acid produced during the first stage of it being turned to no account. In time, a demand grew up for chlorine, that hydrochloric acid began to be utilized, and the manufacturers of Leblanc soda now sent into the market two products, by each of which they gained profits. Then their soda ceased to be profitable, and became a kind of by-product, which they continued to make only because they could not otherwise make chlorine. Now, Leblanc soda gives no profit at all, and chlorine none to speak of; and both have come to be regarded as secondary products, to be made only incidentally, and only because making them is essential to the application to certain ores of the wet method of extracting copper.

Returning to the ammonia process, when that process first began to threaten them, the makers of Leblanc soda comforted themselves by two considerations: one of which was that the ammonia process must itself tend to check its own extension, by reason of the loss of ammonia inseparable from that process so increasing the demand for ammonia as to materially raise the price of that body. They knew that the constantly increasing demand for ammonia for the purposes for which it was already employed had doubled its price within twenty years; and they thought that every further extension of the ammonia soda process must still further increase the market value of ammonia, until at length the ammonia process would cease to have any advantage over the Leblanc process. So far, however, from that anticipation having been realized, despite the immense extension which the ammonia-soda process has recently undergone, the price of ammonia is now beginning to fall. The delusion that it was impossible to collect the ammonia given off from coke ovens without spoiling the coke is at last giving way before accomplished facts. Ammonia is now being obtained commercially, not only from coke ovens, but also from another source, wholly unforeseen and unexpected; and the time, moreover, seems at last to have dawned when there will be collected and utilized as ammonia at least a portion of the nitrogen of nearly all the fuel burnt either for industrial or for domestic purposes. In France ammonia has been collected from coke ovens for a number of years past.

Mr. William Ferrie was struck by the idea that the methods employed for separating ammonia and tar from crude illuminating gas might be used for separating the same bodies from the gases from blast furnaces in which raw coal is used; and although the volume of the gases from such furnaces, per ton of coal employed, is about thirteen times greater than that of the gases obtained by distilling the same kind of coal in retorts—is not less, that is to say, than 130,000 cubic feet—Mr. Ferrie's idea has been put into execution with complete success. From two of the sixteen blast furnaces at the Gartsherrie Ironworks ammonia and tar have been regularly collected for some months past, and the preparations are in progress for collecting them from the other fourteen blast-furnaces there. The quantity of ammonia at present being obtained at Gartsherrie is the quantity corresponding to about 18 cwt. of ammonium sulphate per day, being at the rate of 20 lb. of ammonium sulphate per ton of coal consumed.

Each of the one hundred and twenty Scotch blast-furnaces consumes, on an average, fifty tons of coal per twenty-four hours. The total quantity of coal consumed in them per annum is thus $50 \times 120 \times 365 = 2,190,000$ tons. The quantity of ammonia yielded per ton of coal being, as I have said, the quantity corresponding to 20 lb. of ammonia sulphate, there can thus be obtained per annum from these 120 blast-furnaces a quantity of ammonia corresponding to nearly 20,000 tons of ammonium sulphate, worth, at the present selling price of that commodity, not less than £400,000.

Large, however, as is this quantity, it is only one-tenth of the further quantity which can be obtained from English coke ovens. The quantity of coal coked annually in England is not far short of 20,000,000 tons, and if Mr. Jameson's system were applied to the whole of our coke ovens, with the result of collecting, per ton of coal treated, the same quantity of ammonia as is obtained from the Gartsherrie blast-furnaces, there would be obtained from this source per annum the quantity of ammonia corresponding to 180,000 tons of ammonium sulphate, at present worth more than three and a half millions sterling. Nor is even this all; for I shall have to speak in a moment of another possible, and I believe probable, source of ammonia, even more extensive still.

Now, of the ammonia employed by the ammonia soda-maker, he loses from one-fiftieth to one-fortieth part. As he has to employ from one and a half to one and three-quarter equivalents of ammonia for each equivalent of sodium carbonate finally obtained, we may take it that he loses about one twenty-third of an equivalent of ammonia for each equivalent of sodium carbonate manufactured. In terms of ammonium sulphate, being the terms in which the loss of ammonia in the ammonia-soda process is usually stated, this loss corresponds to about five and a half parts of ammonium sulphate per hundred parts of sodium carbonate produced. The total annual loss of ammonia in the manufacture of the 163,000 tons of ammonia soda now being produced per annum thus corresponds to just about 9000 tons of ammonium sulphate. This is no doubt a large quantity of a commodity worth £20 per ton; but, in comparison with the extent of the new sources of ammonia which have just begun to be turned to account, it is utterly insignificant. It is less than one-twentieth part of the quantity capable of being yielded by blast-furnaces and coke ovens in Great Britain alone, and is a smaller fraction still of the quantity which, I believe, can be obtained from another source which has yet to be mentioned. We may therefore be quite certain that the progress of the ammonia soda process will not be hindered or limited by any difficulty as regards supply of ammonia.

The other consideration to which I referred as having given comfort to the makers of Leblanc soda, and which constituted indeed their chief ground of hope for salvation against the ammonia process, was that the world requires chlorine as well as soda, and that while the chlorine of the salt decomposed by the Leblanc process is yielded as hydrochloric acid, from which free chlorine can be obtained readily, the chlorine of the salt decomposed by the ammonia process is yielded as a somewhat dilute solution of calcium chloride. It was thought that the ammonia process would eventually even help the existing Leblanc soda-makers, by preventing the further extension of the Leblanc process, and so restricting the production of hydrochloric acid, and thereby at length increasing the value of that body. The ammonia process, no doubt, would have produced that result, and would have produced it by this time, if the supply of hydrochloric acid in this country had not been already so largely in excess of the demand for chlorine products. That demand is always becoming larger, and within the last few years the production of hydrochloric acid has appreciably diminished; but in this country the constantly increasing stringency of legislative enactments with respect to river and air pollution has compelled so many producers of hydrochloric acid, who would have preferred to throw their acid away, to employ it in the manufacture of chlorine, whether that manufacture were profitable or not, that the selling price of chlorine products has of late years been continually falling, until it is now at a point at which it barely pays their cost. No doubt, if all the other conditions of the problem were to remain as at present, the demand for chlorine products would in time overtake the supply of hydrochloric acid in this country, as it has long since done on the Continent, and the manufacture of chlorine in England would so again become profitable. But the other conditions of the problem are not likely to remain stationary, and both M. Solvay and myself are doing our best to change them.

M. Solvay is proposing to manufacture hydrochloric acid from the residual calcium chloride of the ammonia process. I imagine that he is urged to that course, not merely by a desire to turn that calcium chloride to account, but also by a desire to avoid making too much nuisance. Neither calcium chloride nor sodium chloride will do much harm to a river, if sent into it in moderate quantities; but when it comes to sending into a comparatively small stream, far inland, 260 tons of calcium and sodium chlorides per twenty-four hours—say about ten tons per hour, night and day, all the year through, and M. Solvay must be doing something very like that at Dombasle—the matter assumes quite another aspect.

Be all that, however, as it may, M. Solvay is now erecting at Dombasle apparatus for an industrial trial of a process for obtaining hydrochloric acid from calcium chloride, at which he has been working for many years. The process in question consists in first concentrating by evaporation the mixed solution of calcium and sodium chlorides which is the residual product of the ammonia process; then mixing the concentrated solution with clay, making the mixture into balls, and drying these balls; and then heating these balls to redness in a current of steam. This process certainly works, on condition that the temperature employed be sufficiently high, and that the quantity of steam used be largely in excess of the quantity necessary to react upon the calcium chloride. As the resulting mixture of vapor and water and vapor of hydrochloric acid would otherwise give an extremely dilute aqueous acid, M. Solvay proposes to separate from it most of its vapor of water, before condensing its hydrochloric acid, by passing the mixture of the two vapors through a very strong solution of $CaCl_2$, which he finds will absorb most of the steam from such a mixture, allowing the HCl to pass on alone, so that it can afterwards be condensed in the usual way. All this is ingenious, but it can hardly be cheap. First, a solution, containing only about eight per cent. of calcium chloride has to be evaporated, we might say to dryness; then the mixture of $CaCl_2$ and clay has to be maintained at a red heat for a considerable time in a current of steam; and then the solution of calcium chloride used to separate steam from the resulting mixture of steam and HCl has to be prepared for use again by having all the water which it has absorbed evaporated off from it. To English manufacturers who have more hydrochloric acid than they can use, this process of M. Solvay's will seem little less than ridiculous; but one must remember that it is intended for countries in which the demand for hydrochloric acid exceeds the supply, and in which countries, moreover, chlorine products are protected by import duties. In such countries one can quite conceive its being commercially practicable: in which case the exportation of chlorine products from England to the Continent is doomed. I ought to add that M. Solvay expects that the silico-aluminate of calcium, which remains after the chlorine of his mixture of calcium chloride and clay has been driven off by steam, will be useful as a cement, and will thus help to pay the cost of his hydrochloric acid.

The exportation of chlorine products from England to the Continent is, moreover, threatened in another way. The continental manufacturers of Leblanc soda, unlike the English manufacturers of Leblanc soda, do not produce enough hydrochloric acid to meet the demand of their respective countries for that acid itself and the products which are made from it. This is partly due to the production of ammonia soda, proportionately to the total production of soda, being so much greater in France and Germany than in this country, and partly to hydrochloric acid being required in those countries for industries which in this country do not exist. Large quantities of chlorine products consequently go to the Continent from this country: our production of hydrochloric acid being still sufficient to enable us to supply not only the total English demand for chlorine and the total American demand for chlorine, but also an appreciable proportion of the Continental demand for chlorine, and, in addition to all that, to throw a large residue of hydrochloric acid into the North Sea. The Continental Leblanc soda-makers do not like this importation into their respective countries of chlorine products from England; but they can prevent it only in one or other of two ways: either by increasing their production of hydrochloric acid, or by becoming enabled to obtain from a given quantity of hydrochloric acid a larger proportion of free chlorine than is yielded by the process at present in use. Personally, I have for the process at present in use that respect which one always feels for the bridge which has carried one over, but I am well aware that it can by no means be regarded as final. It yields chlorine cheaply; but it yields only one-third of the total chlorine contained in the acid employed, the other two-thirds being lost as calcium chloride. English chlorine manufacturers will regard almost with horror the idea of a new chlorine process which shall yield in the free state practically the whole of the chlorine contained in the acid employed; but on the Continent there is a demand for such a process—a demand which will no doubt be lessened, but will by no means be destroyed, by what is being done in France by the Compagnie d'Exploitation—and I am one of those who have been called upon to endeavor to supply that demand. M. Pechiney is now preparing to make at Salindres a trial on an industrial scale of a process which, I think, will supply it; and by the end of this year he will probably have obtained decisive results.

As regards the English chlorine industry, however, I do not think that its prospects are by any means so gloomy as, from what I have said so far, might at first blush appear. But I think that its salvation will come from an unexpected quarter. I think that our English manufacturers of Leblanc soda will have to cease to devote their hydrochloric acid—when they do not throw it away—exclusively to chlorine making. They would, of course, be only too glad to do so, if a means could be furnished them of turning it to account otherwise. But the difficulty hitherto has been as to how to turn it to account otherwise. I believe that that difficulty is about to disappear. I am not free to enter into that matter now, and, indeed, it is not yet ripe for discussion; but I have very great confidence that new applications of hydrochloric acid, admitting of being applied very extensively, at comparatively small expense, are among the things of the immediate future.

There has come to me from Newcastle a very bold, but I venture to think, quite practical suggestion, the result of which can hardly fail to be of enormous importance, not only to the soda industry but to almost all industries whatever. That suggestion is that the soda-maker should entirely cease to use raw coal as fuel, but should convert all his coal into coke, collecting for sale the oil and ammonia evolved during its conversion into coke, and himself using for heating purposes the gases evolved during the coking operation and the coke itself. It is believed that, in the Newcastle district at any rate, by this mode of proceeding the soda-maker would obtain his fuel virtually for nothing. In that district there is produced per annum some two millions of tons of very small coal or "duff," which is almost a waste product, and which, singularly enough, yields more oil than the more costly kinds of Newcastle coal, while at the same time yielding a very fair coke, sufficiently good, at any rate, for use in the furnaces of chemical works, especially when its combustion is assisted by that of the gases from the ovens in which the coke is produced; and the value of the oil and ammonia obtained when this "duff" is coked in ovens to which the Jameson system is applied is greater than the cost of the "duff" *plus* the cost of coking it. And it is probable that improved condensing arrangements will render the yield, if not of oil, at any rate of ammonia, so much greater than the yield hitherto actually realized, as to enable the same result to be obtained in the case of ordinary steam coal, not only in the Newcastle district but in the Lancashire district also. If so, the cost of producing Leblanc soda in both districts will be diminished by almost the total amount of the present cost of Leblanc soda for fuel. I say "almost," because, so far as one can see, the use of raw coal for "mixing" in the black ash process must still be continued.

And it seems to me that this idea cannot but be as applicable to almost all other industries as to the soda industry, while the result to the material well-being of mankind of its general application it is utterly beyond the power of any imagination adequately to conceive. This idea means, among other things, cheaper fuel for all purposes, an enormously increased supply of agricultural produce, and the entire suppression of smoke, even in the busiest centres of industry.

And for my own part I venture to think that the same idea might be applied even to the fuel required for domestic purposes, rendering London absolutely free from smoke, and pea-soup fogs things only of tradition. I think that the time will come when our gasworks will be replaced, at least to a large extent, by establishments in which coal will be treated for the production of coke, illuminating oils, ammonia, and heating gases; the coke to be burnt in our domestic fire-places, the oils to be used for lighting the interiors of our houses, the ammonia to be employed in agriculture, to cheapen and render more abundant our supplies of food, and the gases to be burnt for raising steam for driving dynamos for lighting our streets by the electric arc.

RECENT RESEARCHES ON THE PYRIDINE AND QUINOLINE BASES.

Ever since it was shown that a close connection exists between some of the important natural alkaloids and the derivatives of pyridine and quinoline, researches intended to aid in determining the nature and relationships of these derivatives have become more and more numerous, and at present the greatest activity prevails in this field of chemistry. All the evidence accumulated thus far is in harmony with the view that many of the important alkaloids are derivatives of pyridine, in the same sense that the so-called aromatic compounds are derivatives of benzene; and as the study of the isomeric derivatives of benzene has led to important synthetical results, so similar work in the pyridine series will probably lead to the synthesis of some of the alkaloids.

Pyridine Series, $C_nH_{2n-5}N$.—These bases were discovered by Anderson in bone oil, and found by Thenius to be present in coal tar. Cahours and Etard, in 1880, succeeded in obtaining them from nicotine by dry distillation. As thirty years had elapsed since the time of Anderson's work, and these bases had in the meantime assumed a considerable degree of importance, Richard and Weidel, and Herzig again undertook the study of bone oil. As a result of their labors we now know that, besides pyridine, there are present in bone oil two isomeric picolines, two lutidines and two collidines. Perkin, in 1865, first observed the artificial production of pyridine by the action of nascent hydrogen on azodinaphthyldiamine, and since then the synthesis of this base has been frequently attempted. Methods have been described by Chapman and Smith, by Ramsay, and more recently by Königs, which yield small quantities of pyridine, but for its preparation in quantity we are still dependent upon bone oil. To obtain pyridine and its homologues, bone oil is warmed with dilute sulphuric acid, the filtered solution precipitated with sodium hydroxide, and the free bases separated by fractional distillation.[1] The most rapid method of obtaining pure pyridine is to distil the calcium salt of nicotinic acid with lime.[2] Of the three picolines theoretically possible Weidel has found two in bone oil, while Baeyer[3] has made a third by the distillation of acroleïn-ammonia. Lutidine had not been made synthetically until very recently. Hantzsch[4] describes a method which enabled him to make the first four members of this series of bases. By heating acetoacetic ester with aldehyde-ammonia in the proportion of two molecules of the former to one of the latter, there is formed a crystalline condensation-product which is the ester of dihydro-collidine-dicarbonic acid $(C_2H_5OOC)_2C_8H_{11}N.H_2$. By the oxidizing action of nitrous acid two atoms of hydrogen are removed, and there remains the ester of collidine-dicarbonic acid. This by saponification yields the corresponding acid, which when distilled with lime gives collidine,

$$\underset{\text{Collidine-dicarbonic acid.}}{C_5(CH_3)_3(COOH)_2N} - 2CO_2 = \underset{\text{Collidine.}}{C_5(CH_3)_3H_2N}.$$

By careful oxidation with potassium permanganate, collidine dicarbonic acid yields three successive oxidation products, each of which in turn can be converted into its corresponding base. Thus the first oxidation product gives lutidine,

$$\underset{\text{Lutidine-tricarbonic acid.}}{C_5(CH_3)_2(COOH)_3N} - 3CO_2 = \underset{\text{Lutidine.}}{C_5(CH_3)_2H_3N};$$

the second, picoline,

$$\underset{\text{Picoline-tetracarbonic acid.}}{C_5(CH_3)(COOH)_4N} - 4CO_2 = \underset{\text{Picoline.}}{C_5(CH_3)H_4N};$$

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[1] Richard, Bulletin de la Société Chimique, **32**, 487.

[2] Laiblin, Annalen der Chemie, **196**, 159.

[3] *Ibid.* **155**, 283.

[4] *Ibid.* **215**, 1.

and the third, pyridine,

$$\underset{\text{Pyridine-pentacarbonic acid.}}{C_5(COOH)_5N} - 5CO_2 = \underset{\text{Pyridine.}}{C_5H_5N.}$$

Other methods for the preparation of collidine are known. Baeyer and Ador[1] have obtained it by heating an alcoholic solution of aldehyde-ammonia to 120°. Krämer,[2] by heating ethylidene chloride with alcoholic ammonia, observed its formation; while more recently Würtz[3] obtained it by the distillation of aldol-ammonia. The higher members of this series, parvoline, corridine, rubidine and viridine, have not yet been made synthetically.

The hypothesis of Körner, according to which the pyridine molecule is regarded as benzene in which one of the six CH groups is replaced by an atom of nitrogen, has found additional support during the last three years. Accepting this hypothesis, but one pyridine is theoretically possible, and indeed it has been found that from whatever source obtained, whether from bone oil, from coal tar or from nicotine, cinchonine or quinoline, pyridine always has the same boiling point, the same specific gravity and the same physical and chemical properties. Picoline, the second member of the series, being regarded as a methyl derivative of pyridine, three isomers are possible, and corresponding to each there should be a pyridine-monocarbonic acid. Three picolines are known, and Weidel and Herzig[4] obtained the third pyridine monocarbonic acid possible by heating lutidinic acid. Nine lutidines are predicted by theory, six dimethyl- and three ethyl-pyridines. Only two of the former are known. On the other hand, six pyridine-dicarbonic acids have been isolated. We can conceive of the formation of collidines by replacing the hydrogen of pyridine either by three methyl groups, by one propyl group, one isopropyl group, or by one methyl and one ethyl group. There are thus possible six trimethyl pyridines, three propyl pyridines, three isopropyl pyridines and ten methyl ethyl pyridines; in all, twenty-two collidines. A number of these are already known, but our knowledge of their properties, physical constants, and especially their oxidation products, is so limited that at present it is impossible to classify them.

The homologues of pyridine and of quinoline, as well as quinoline itself and certain natural alkaloids, such as quinine, cinchonine, nicotine, etc., when oxidized yield nitrogenous acids, which may be regarded as carboxyl derivatives of pyridine. Distilled with lime they give pyridine just as benzoic, phthalic acids, etc., under the same conditions give benzene. Pyridine itself offers a much greater resistance to oxidizing agents than benzene; chromic acid, and even boiling fuming nitric acid have no effect upon it. Huber first obtained nicotinic acid (pyridine monocarbonic acid) by oxidizing nicotine, and in 1871 Dewar obtained the same acid by the oxidation of a picoline. By oxidizing the mixture of picolines contained in bone oil Weidel[1] obtained two isomeric pyridine monocarbonic acids, which he calls nicotinic and picolic acids, and by oxidizing lutidine Weidel and Herzig[2] succeeded in isolating the third isomer possible, which they call isonicotinic acid. Wischnegradsky[3] oxidized the aldehyde collidine of Baeyer, and obtained a methyl-pyridine-dicarbonic acid; while Hoogewerf and van Dorp[4] have obtained pyridine tricarbonic acid by oxidizing quinine and cinchonine with potassium permanganate. A second acid of this composition has been obtained by Böttinger[5] from uvitonic acid.

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[1] Annalen der Chemie, **155**, 297.

[2] Berichte der deutschen chemischen Gesellschaft, **3**, 202.

[3] Comptes Rendus, **88**, 454.

[4] Monatshefte für Chemie, **1**, 41.

The pyridine bases have the power of uniting directly with two, four or six atoms of hydrogen. Wischnegradsky[6] has described a hexahydrolutidine which has the properties of a secondary base. The isochlor-pyridine of Ciamician and Dennstedt[7] can also unite with six atoms of hydrogen. Hofmann[8] has devised a general method for building up the hydropyridines. By distilling a mixture of a pyridine ammonium iodide with potassium hydroxide, oxygen is liberated, potassium iodide formed, and the hydrogen of the hydroxide takes the place of the iodine in the base. Thus with the iodide of methyl-pyridylammonium this reaction takes place,

$$\underset{\text{Methyl pyridyl ammonium iodide.}}{C_5H_5N.CH_3I} + KOH = O + KI + \underset{\text{Dihydro-picoline.}}{C_5H_5NCH_3H}$$

As these hydro-bases can be readily transformed into the bases themselves, the reaction of Hofmann becomes the more valuable, because it enables us to pass directly from any member of the series to the next higher.

According to Wischnegradsky the pyridine bases exist in the state of hydrides in the alkaloids. From the labors of Königs[9] and of Schotten[10] we know that piperidine is hexahydropyridine, and more recently Oeschner de Koninck[11] has found tetrahydroquinoline in the crude quinoline obtained by distilling cinchonine with sodium hydroxide. The researches of Cahours and Etard have shown that nicotine is a tetrahydroisodipyridine, while further evidence in favor of this idea is to be found in the work of Weidel and Russo.[12] Starting with pyridine C_5H_5N, treating with metallic sodium, they obtained dipyridyl $C_{10}H_8N_2$. Treated with nascent hydrogen dipyridyl takes up six atoms, and there is formed isonicotine, $C_{10}H_{14}N_2$.

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[1] Berichte der deutschen chemischen Gesellschaft, **12**, 1989.
[2] Monatshefte für Chemie, **1**, 48.
[3] Berichte der deutschen chemischen Gesellschaft, **12**, 1506.
[4] Annalen der Chemie, **204**, 84.
[5] Berichte der deutschen chemischen Gesellschaft, **13**, 2048, and **14**, 134.
[6] Bulletin de la Société Chimique, **34**, 340.
[7] Berichte der deutschen chemischen Gesellschaft, **14**, 1153. [8] *Ibid.* **14**, 1497. [9] *Ibid.* **12**, 2341.
[10] *Ibid.* **15**, 421. [11] Annales de Chimie et de Physique (5), **27**, 433.
[12] Monatshefte für Chemie, **3**, 850.

A number of substitution products of pyridine are known. Hofmann, Anderson and Ciamician and Dennstedt have described chlorine and bromine derivatives. O. Fischer[1] obtained pyridinesulphonic acid by heating pyridine with an excess of concentrated sulphuric acid, and from this, by means of well-known reactions, he prepared the cyanide and the corresponding acid.

Quinoline Series, $C_nH_{2n-11}N$.—By distilling quinine, cinchonine or strychnine with potassium hydroxide, Gerhardt[2] obtained a substance having the properties of an energetic base which he called quinoline. Two years previous, in 1843, Runge had discovered leucoline, a base of the same composition occurring in coal tar. Hofmann[3] finding that leucoline and quinoline gave the same crystalline precipitate with chromic acid, concluded that the two bases were identical. The study of these compounds was undertaken in 1860 by C. G. Williams, and he succeeded in isolating the parallel series of homologous bases as follows:

Quinoline,	C_9H_7N	Leucoline.
Lepidine,	$C_{10}H_9N$	Iridoline.
Dispoline,	$C_{11}H_{11}N$	Cryptidine.
Tetrahiroline,	$C_{12}H_{13}N$	

By the decomposition of the alkaloids with caustic potassa, bases of the first series are exclusively formed, while the members of the second series occur in coal tar. In properties these bodies resemble the pyridine bases. Towards alkyl iodides they act like tertiary amines, and on oxidation they are transformed into pyridine carbonic acids. Pure quinoline, free from its homologues, may be prepared by heating cinchonine with copper oxide and caustic potassa.[4] Königs[5] has made it synthetically by passing the vapor of allyl-aniline, $C_6H_5NHC_3H_5$, over heated lead oxide. Baeyer[6] by treating hydrocarbostyril with phosphorus pentachloride, obtained dichlorquinoline, which by nascent hydrogen was converted into quinoline. The dry distillation of acridate of calcium, or of acroleïn-aniline, also yields quinoline.[7] Böttinger[8] states that the hydrochlorate of aniluvitonic acid when heated with soda lime is converted into quinoline. But these methods are only of scientific interest, and it is to the work of Skraup[9] that we owe a process for the synthesis of quinoline and its homologues which is not only of the greatest theoretical value and of general application, but at the same time it is an economical method for the production of these bases in quantity. The details of the process have been described in a previous volume of this Journal.[10]

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[1] Berichte der deutschen chemischen Gesellschaft, **15**, 62.

[2] Annalen der Chemie, **42**, 310, and **44**, 279.

[3] *Ibid.* **53**, 427.

[4] Wischnegradsky, Berichte der deutschen chemischen Gesellschaft, **13**, 2318.

[5] *Ibid.* **12**, 453.

[6] *Ibid.* **12**, 1320.

[7] Graebe and Caro, *Ibid.* **13**, 99.

[8] *Ibid.* **13**, 2165.

[9] Monatshefte für Chemie, **1**, 316, and **2**, 139 and 171.

[19] See this Journal, **4**, 63.

The synthesis of lepidine, the second member of the series, has been effected by Döbner and Miller.[1] The method is analogous to that of Skraup, and consists in heating a mixture of aniline, nitrobenzene, sulphuric acid and glycol or paraldehyde.

The quinoline bases when oxidized are transformed into pyridine-carbonic acids, quinoline itself yielding cinchomeronic acid or pyridine-dicarbonic acid. This fact indicates a close connection between the quinoline bases and such alkaloids as quinine, cinchonine and their isomers, because these two when oxidized are converted into pyridine di or tricarbonic acids. Quinoline, like the pyridine bases, has the power of forming hydrides by treatment with tin and hydrochloric acid. Wischnegradsky[2] obtained from it tetrahydroquinoline, and Jackson[3] has also described a tetrahydroquinoline, both of which are secondary bases. They are very unstable substances, and the weakest oxidizing agents change them back into quinoline.

Among the substitution-products of quinoline are the oxyquinolines or quinophenols analogous to the naphthols in their mode of formation, properties and general reactions. Nitroquinoline, like nitronaphthalene, readily yields the amine, and the cyanogen derivatives can be transformed in the usual way into the quinoline-carbonic acids. In fact, the synthesis of quinoline and the analogies existing between its derivatives and those of naphthalene seem to justify Körner's structural formula. According to his hypothesis quinoline has a structure analogous to that of naphthalene, and bearing the same relation to pyridine that naphthalene does to benzene; and as one of the CH groups of naphthalene is supposed to be replaced by an atom of nitrogen, we see the possibility of two such substances corresponding with the α and β monosubstitution products of naphthalene. Because of its formation from dichlorquinoline Baeyer regards quinoline and its homologues as belonging to the α series; leucoline and its homologues would hence belong to the β series. But it is still an open question whether leucoline is really isomeric with quinoline. Hofmann regarded them as identical, but C. G. Williams pointed out that quinoline with amyl iodide yields the blue coloring matter cyanine, while leucoline has not this property. Hoogewerf and Van Dorp[4] have confirmed the statement of Williams; but, on the other hand, quinoline and leucoline when oxidized with potassium permanganate give the same pyridine-dicarbonic acid.

E. H. K.

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[1] Berichte der deutschen chemischen Gesellschaft, **14**, 2812.

[2] Bulletin de la Société Chimique, **34**, 340.

[3] Berichte der deutschen chemischen Gesellschaft, **14**, 889.

[4] Annalen der Chemie, **204**, 117.

Researches on Caffeïne.

Although, since the celebrated work of Liebig and Wöhler, uric acid has been a frequent subject of investigation, a comparatively small amount of study has been devoted to the allied bases, caffeïne, theobromine, xanthine and guanine. In the hope now of throwing light on the nature of uric acid Emil Fischer[1] has undertaken a careful study of caffeïne and has reached results of considerable interest and importance. An abstract of Fischer's paper is here given.

That some connection exists between uric acid and caffeïne was shown by the early investigations of Stenhouse[2] and of Rochleder.[3] By oxidizing caffeïne with nitric acid the former obtained nitrotheïne or cholestrophane, which was afterward recognized as dimethyl-parabanic acid. He also observed in the same reaction the formation of a substance which yielded a purple color with ammonia, similar to that of murexide. Rochleder investigated the conduct of caffeïne towards moist chlorine, and discovered chlorcaffeïne and amalic acid. He was struck by the similarity of this substance to alloxantin, and Strecker showed it to be a methyl derivative of alloxantin. This observation of Rochleder forms the basis of Fischer's investigation.

The principal new facts established are the following:

1. By careful oxidation with chlorine, caffeïne yields dimethyl-alloxan and methyl-urea:

$$\underset{\text{Caffeïne.}}{C_8H_{10}N_4O_2} + 2O + 2H_2O = \underset{\text{Dimethyl-alloxan.}}{C_6H_8N_2O_5} + \underset{\text{Methyl-urea.}}{C_2H_6N_2O}.$$

2. By reduction with hydrogen sulphide, dimethyl-alloxan yields amalic acid (tetramethyl-alloxantin); and this by careful oxidation with nitric acid again yields dimethyl-alloxan.

3. There is one atom of hydrogen in caffeïne which differs from the others in being easily replaced by the ordinary substituting groups. Among the products described is hydroxy-caffeïne, $C_8H_9(HO)N_4O_2$.

4. Caffeïne easily takes up two atoms of bromine, forming an addition-product. Hydroxy-caffeïne acts in the same way. If the latter action takes place in the presence of alcohol, a diethoxy-derivative is formed, thus:

$$\begin{gathered} C_8H_9(HO)N_4O_2 + 2C_2H_6O + 2Br \\ = 2HBr + C_8H_9(HO).N_4O_2(OC_2H_5)_2. \end{gathered}$$

5. Diethoxy-hydroxy-caffeïne, when treated with warm hydrochloric acid, is converted into two new bodies, apo-caffeïne, $C_7H_7N_3O_5$, and hypo-caffeïne, $C_6H_7N_3O_3$.

6. Apo-caffeïne, $C_7H_7N_3O_5$, when boiled with water, yields carbon dioxide and caffuric acid:

$$\underset{\text{Apo-caffeïne.}}{C_7H_7N_3O_5} + H_2O = CO_2 + \underset{\text{Caffuric acid.}}{C_6H_9N_3O_4}$$

Annalen der Chemie, **215**, 253. [2] *Ibid.* **45**, 366; and **46**, 272. [3] *Ibid.* **69**, 120; and **71**, 1.

7. Caffuric acid is decomposed when heated with basic acetate of lead, yielding mesoxalic acid, methylamine and methyl-urea:

$$\underset{\text{Caffuric acid.}}{C_6H_9N_3O_4} + 3H_2O = \underset{\text{Mesoxalic acid.}}{C_3H_4O_6} + \underset{\text{Methyl-amine.}}{CH_3NH_2} + \underset{\text{Methyl-urea.}}{C_2H_6N_2O}$$

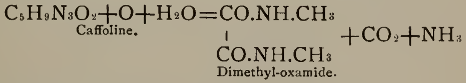
8. When treated with fuming hydriodic acid, caffuric acid is converted into hydro-caffuric acid, $C_6H_9N_3O_3$, which breaks up into methylamine and an acid which in turn readily yields methyl-hydantoïne, $C_4H_6N_2O_2$, and carbon dioxide. This series of transformations indicates that in caffeïne there is not only the alloxan nucleus, but also the carbon-nitrogen nucleus of methyl-hydantoïne.

9. Hypo-caffeïne, $C_6H_7N_3O_3$ (see 5), is broken up, when heated with water at 150°, or when treated with bases at a lower temperature, yielding carbon dioxide and caffoline, $C_5H_9N_3O_2$; and this, treated with hydriodic acid, yields methyl-urea and another product.

10. Caffoline, $C_5H_9N_3O_2$, is converted into methyl-oxamic acid and methyl-urea when oxidized with an alkaline solution of potassium ferricyanide:

$$\underset{\text{Caffoline.}}{C_5H_9N_3O_2} + O + H_2O = \underset{\text{Methyl-oxamic acid.}}{CH_3.NH.CO.CO_2H} + \underset{\text{Methyl-urea.}}{CH_3.NH.CONH_2}$$

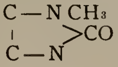
With an alkaline solution of potassium permanganate it yields dimethyl-oxamide:

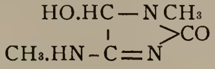


$$\underset{\text{Caffoline.}}{C_5H_9N_3O_2} + O + H_2O = \underset{\text{Dimethyl-oxamide.}}{\begin{array}{l}CO.NH.CH_3\\ \quad |\\ CO.NH.CH_3\end{array}} + CO_2 + NH_3$$

Chromic acid converts it into cholestrophane:

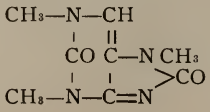
$$\underset{\text{Caffoline.}}{C_5H_9N_3O_2} + O = \underset{\text{Cholestrophane.}}{C_5H_6N_2O_3} + NH_3.$$

These transformations lead to the conclusion that in caffoline the group,  $\begin{array}{l}C-N\,CH_3\\ | \qquad\quad >CO\\ C-N\end{array}$, is present, and that its formula is



$$\begin{array}{l} \qquad HO.HC-N\,CH_3 \\ \qquad\qquad\quad | \qquad\ >CO \\ CH_3.HN-C=N \end{array}$$

Taking all the above facts and conclusions into consideration, Fischer suggests as the formula of caffeïne,



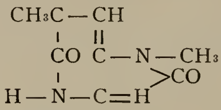
$$\begin{array}{l} CH_3-N-CH \\ \qquad\quad |\quad\ \ \| \\ \qquad\ CO\ \ C-N\,CH_3 \\ \qquad\quad |\quad\ \ | \qquad\ >CO \\ CH_3-N-C=N \end{array}$$

A careful examination of this formula will show that it is what it ought to be, and nothing more, an expression in chemical language of facts previously established.

Theobromine, the lower homologue of caffeïne, may be transformed into the latter by the introduction of a methyl group. But as caffeïne contains three methyl groups united to nitrogen, the question remains open, which one is lacking in theobromine. By oxidation with chromic acid, dimethyl-parabanic acid is obtained from caffeïne, and mono-methyl-parabanic acid from theobromine.

When treated with chlorine, caffeïne breaks up into mono-methyl-urea and dimethyl-alloxan, while theobromine yields mono-methyl-alloxan.

Only one methyl group in theobromine is, therefore, in the alloxan nucleus; and since it is split off in forming apo- and hypo compounds, it is the one indicated by (*a*) in the formula for caffeïne. The formula for theobromine is therefore



$$\begin{array}{llll} CH_3C & - & CH & \\ \quad | & & \| & \\ \quad CO & & C - N - CH_3 & \\ \quad | & & & >CO \\ H - N & - & C = H & \end{array}$$

The similarity of xanthine to theobromine was noticed by Strecker some time ago, but he was unable to transform it into one or the other by adding methyl. But Fischer has effected the synthesis of theobromine by treating the lead compound of xanthine with methyl iodide. He has also shown that the action of chlorine on xanthine is analogous to the action of chlorine on caffeïne and theobromine, urea and alloxan being formed. This fact furnishes the desired experimental demonstration that theobromine is the dimethyl, and caffeïne the trimethyl, derivative of xanthine. D. T. D.

NOTES.

On the Oxidation of Cork Stoppers and Rubber Joints.[1]

Dear Sir : The remarks of Keiser and yourself[2] on a source of error in experimentation due to the formation of carbon dioxide by the action of ozone on cork stoppers and rubber connecters, of the apparatus employed, suggest to me that I have too long neglected to bear witness to the accuracy of the observation of H. Karsten, to the effect that such connecters are constantly liable to oxidation even in mere air and at the ordinary temperature. In a paper "On the extreme difficulty of removing the last traces of carbonic acid from large quantities of air," published in 1860 by C. W. Eliot[1] and myself, we remarked incidentally that Karsten had apparently not allowed for this particular difficulty in some experiments published by him[2] in that year "On the action of oxygen on non-nitrogenous organic substances," to which criticism Karsten made reply[3] by suggesting that we were ourselves at fault in not having allowed for the contact of air with the organic matter of the corks and connecters of our apparatus. He described experiments, withal, by which the presence of carbonic acid was exhibited in air that had been passed through rubber tubing, and verified his earlier work by performing similar experiments in apparatus specially designed to avoid this source of error. At the first opportunity that presented itself to me, which was not until 1870, I repeated Karsten's experiment and satisfied myself of the entire accuracy of it. For example, on pushing, slowly, 179,500 cc. of air through the apparatus described by Karsten, absolutely no precipitate of carbonate of lime was obtained in the lime water, nor was any precipitate formed when 150,000 cc. of air were drawn through the apparatus by means of an aspirator. The apparatus in question is arranged in such manner that all the connecters are shielded from contact with the air. Moreover, the air was passed through ignited oxide of copper, to destroy oxidizable carbonaceous matters before it came to the potash bulbs proper to remove carbonic acid at the anterior part of the apparatus. *Per contra*, I did obtain precipitates of calcic carbonate in the lime water on aspirating the purified air through the apparatus arranged as just now described, with the exception that its joints were not specially protected from contact with air. Under these conditions 150,000 cc. of the air gave a slight precipitate, and 180,000 cc. gave a considerable precipitate.

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[1] A letter to the Editor.

[2] Remsen and Keiser, this Journal, **4**, 456.

It follows, of course, that if cork stoppers can be slowly oxidized by mere air, they must in certain cases be carefully protected from ozone, as the experiments of Keiser and yourself have so clearly shown. Karsten[4] found a fourfold increase in the yield of carbonic acid when his non-nitrogenous substances were exposed to air ozonized by phosphorus, instead of to ordinary atmospheric air.

F. H. STORER.

BUSSEY INSTITUTION, JAMAICA PLAIN, MASS., *April* 2, 1883.

Carbonic Acid.

M. BALLO has endeavored to answer the question whether the hypothetical carbonic acid is present in solutions of carbon dioxide in water, by introducing into such solutions pieces of magnesium ribbon. He first showed that magnesium does not act upon water itself, even at the boiling temperature. On then introducing the metal into carbonic acid, a slow evolution of hydrogen soon began at the ordinary temperature and continued regularly for some time. The facts that at ordinary temperatures a large amount of carbon dioxide remains in solution in water and that there is a gradual decomposition, are in accordance with the assumption that there is actually a compound present. Acid carbonates in solutions also dissolve magnesium.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 3003.)

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[1] Proceedings of the American Academy, **5**, 62.

[2] Poggendorf's Annalen, **109**, 346.

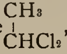
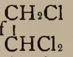
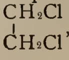
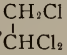
[3] *Ibid.* **115**, 348.

[4] *Ibid.* **109**, 351.

The Atomic Refraction of Sulphur.

R. Nasini has studied a number of sulphur compounds with reference to their refractive power, and has found that sulphur has at least two refractive equivalents. Brühl[1] has shown that carbon, in the usual condition of combination, has one refractive equivalent, and in the condition called "double linkage" another; and that oxygen also has two values according to whether it is present in a compound in the hydroxyl condition or the carboxyl condition. The results obtained by Nasini for sulphur are similar to those obtained by Brühl for carbon and for oxygen. The number of sulphur compounds studied is limited, so that the values given do not depend upon as many accurate measurements as do those for carbon and oxygen. In such compounds as ethyl mercaptan, $C_2H_5(SH)$, ethyl sulphide, $(C_2H_5)_2S$, etc., the refractive equivalent is 7.65; while in such as CS_2 and $CS(OC_2H_5)_2$ it is 8.84.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2878.)

Relations between Boiling Points and Specific Volumes.

W. Staedel has made an elaborate study of the chlorine substitution products of ethane, and has succeeded in showing that simple relations exist between the figures representing the boiling points and those representing the specific volumes. To illustrate the character of the relations a few examples may be cited. The boiling point of the substance  $\begin{array}{c}CH_3\\|\\CHCl_2\end{array}$, under a pressure of 400 mm., is 39.607°; that of  $\begin{array}{c}CH_2Cl\\|\\CHCl_2\end{array}$ is 92.758°. The difference is a fraction more than 53°. That is, an elevation in the boiling point of about 53° is effected by the substitution of the first hydrogen atom in the group CH_3. A number of similar cases show that this is a general rule, so far at least as the compounds examined are concerned. Secondly, the compound,  $\begin{array}{c}CH_2Cl\\|\\CH_2Cl\end{array}$, boils at 64.733° (400 mm. barom.), while the compound, $\begin{array}{c}CH_2Cl\\|\\CHCl_2\end{array}$, boils at 92.758°. Here the difference is about 28°. Thus it will be seen that the introduction of the second chlorine atom into CH_2Cl causes an elevation in the boiling point of 28°. Finally,  $\begin{array}{c}CH_2Cl\\|\\CHCl_2\end{array}$ boils at 92.758° and $\begin{array}{c}CH_2Cl\\|\\CCl_3\end{array}$ at 108.127°. The difference is something more than 15°; or by the introduction of the third chlorine atom the boiling point is raised about 15°. All the possible illustrations of these regularities furnished by the chlorine products of ethane are studied and the rules above given found to be true in all cases except one. Similar regularities were observed in connection with the specific volumes. The exact values found corresponding to the normal pressure (760 mm.) are here given. For the boiling points,

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[1] See this Journal, **3**, 352.

$$B(cl_1 - h) = 56.22$$
$$B(cl_2 - h) = 31.30$$
$$B(cl_3 - h) = 16.04$$

For the specific volumes,

$$S(cl_1 - h) = 14.20$$
$$S(cl_2 - h) = 16.37$$
$$S(cl_3 - h) = 19.16$$

These equations express the changes in the boiling points (B) and the specific volumes (S) effected by introducing into a substance one chlorine for the first hydrogen $(cl_1 - h)$; a chlorine atom for the second hydrogen $(cl_2 - h)$; and a chlorine atom for a third hydrogen $(cl_3 - h)$.

It appears from these results that a chlorine atom may have different "boiling values" and different specific volumes. Either this is true, or carbon, or hydrogen or both have different values in isomeric compounds. Hence the assumption of the constancy of the specific volumes even of the univalent elements appears somewhat unjustifiable.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2559.)

Estimation of Vapor Densities.

Victor Meyer cautions chemists against too general a use of his simple method for the estimation of specific gravities of vapors, and calls attention to the title of his first paper describing the method. The title is, "On the estimation of vapor densities of bodies boiling above 440°, as well as of bodies which attack mercury or Wood's metal." Meyer says that the use of the method should be restricted to cases in which the exact methods of Gay Lussac, Dumas and Hofmann cannot be used.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2778.)

Note on the Test for Tin mentioned in this Journal, 4, 474.

I find that iron wire works much more satisfactorily than copper. Ferrous chloride does not reduce mercuric chloride. Stannic chloride alone, or in the presence of antimony, or of antimony and arsenic, is reduced to stannous chloride and gives the test with mercuric chloride. Arsenic in the absence of antimony prevents the reduction, but if enough antimony is present so that metallic antimony is precipitated, the stannic chloride will be reduced at the same time. The presence of much arsenic will entirely prevent the precipitation of a little antimony, but tin can be detected after the addition of enough antimony chloride so that metallic antimony is precipitated on boiling with iron. This test is essentially the same as a process given by Fresenius for the quantitative separation of antimony and tin. It is found to work well as a qualitative test in the hands of students, which cannot be said of the usual process, based on the reduction to metallic tin by means of zinc and platinum. W. A. Noyes.

Fermentation of Cellulose.

F. Hoppe Seyler has proved conclusively that in sewage there is a ferment which has the power of converting cellulose into marsh gas and carbon dioxide. A small quantity of sewage, the amount of organic matter in which had been previously determined, was brought into a flask with a known quantity of cellulose and distilled water. The gases given off were carefully measured and analyzed, and it was thus found that the cellulose was certainly transformed into marsh gas and carbon dioxide. The evolution of gases continued thirteen months, and was still in progress. As the ferment involved in this action is found in all kinds of refuse organic matter, this fermentation of cellulose must be going on to an enormous extent on the surface of the earth.—(*Berichte der deutschen chemischen Gesellschaft*, 15, 122.)

Quinoline derivatives in Medicine.

Otto Fischer has recently patented processes for making certain derivatives of quinoline. Oxyquinoline and methoxyquinoline prepared from quinolinesulphonic acid can be converted by reducing agents into tetrahydro-compounds. The tetrahydrides are converted into methyl and ethyl derivatives when treated with the corresponding iodides, and these derivatives are tertiary bases:

$$\underbrace{C_9H_{11}NO}_{\text{Oxyquinoline tetrahydride.}}+CH_3I=HI+C_{10}H_{13}NO$$

β–Oxyhydromethylquinoline crystallizes and forms easily soluble salts. This compound as well as some others similar to it have strong anti-febrile properties, and may be used as satisfactory substitutes for quinine.

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METHODS OF ANALYSING SAMARSKITE

And the other Columbates containing Earthy Oxides, by the Agency of Fluorhydric Acid; and of Dissolving Columbite and Tantalite by the same Acid.—On the Separation of Thoria from the other Oxides.—Quantitative Estimation of Didymium Oxide in its Mixtures with other Earthy Oxides.

By J. Lawrence Smith, *Louisville, Ky.*

[*Concluded from p.* 51.]

Earths from Samarskite.

As it has been necessary to use letters to indicate the various groups of constitutents of this mineral, they will be stated in a list, for easy reference:

A—The portion of samarskite soluble in fluorhydric acid.

B—The portion of samarskite insoluble in fluorhydric acid.

C—The mixed oxalates of the earths from samarskite.

D—The earthy oxides insoluble or dissolved with difficulty by the sulphate of potassium or sodium.

From the time that samarskite was discovered until I undertook the examination of the mineral as it was found in Mitchel county, N. C., the earths from the ignited oxalates were considered to be the oxides of the cerium group and yttria group, and in my researches made in 1876 and 1877, while I referred to one of these oxides as cerium oxide, in a footnote[1] I stated that there were grounds for belief that the oxide so called was not cerium oxide, as it was completely soluble in a very dilute solution of nitric acid.

A little later, by repeated precipitation of this oxide (as prepared from samarskite) with sodium sulphate I obtained an oxide, the sulphate of which is absolutely insoluble in a concentrated solution of the sulphate. The oxide of this was completely soluble in very dilute nitric acid. In many respects it resembled cerium oxide. Among them it did not furnish any absorption ray in the spectrum, but its complete solubility in very dilute nitric acid was a marked distinction between it and cerium oxide. For this reason I considered it a new oxide and called it mosandrum. The atomic weight of the oxide was made out to be 109 ($O = 16$).

M. Marignac, however, as well as Prof. Delafontaine, was inclined to regard the oxide as terbia. The properties of this latter earth were never clearly understood, yet as far as I had been able to make them out I considered it to differ from what I had called mosandrum. Not having any absorption ray, it is not so easy to decide upon as upon most of the earthy oxides.

The study instituted upon the earths coming from samarskite opened a new field of investigation upon the earths of the cerium and yttrium groups, especially among those which gave marked and decided absorption rays. As yet they cannot be separated in a pure state in sufficient quantity for a complete chemical study, at least so far as my information at the present time goes.

Prof. Delafontaine, of Chicago, has done some excellent work on these earths, among which he considers that he has discovered two metals that are new, phillipium[2] and decipium. In regard to the first, the spectroscopic and other characteristics are well defined, so much so that those chemists and physicists who have examined it, as MM. Marignac, Soret and Lecoq de Boisbaudrant, have no doubt upon the subject. As regards decipium,[3] the spectroscopic examination of Soret and Lecoq de Boisbaudrant has not as yet furnished us with any positive decision, as far as my information extends at the present time; M. Delafontaine, however, feels satisfied about it.

In addition to the above, M. Marignac has separated another, working, however, on gadolonite and euxinite, which he calls ytterbium,[4] and L. F. Nilson another, which he calls scandium,[5] and believes to be associated with the ytterbium of Marignac. It is determined by spectroscopic examination of a somewhat complicated nature. I would here state that most of these new earths have only been made out by a very small quantity, sometimes less than a gram, the spectroscopic work being done by the most skillful observers.

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[1] Amer. Jour. Science, May 1877.

[2] Comptes rendus, 1878, **86**, 559.

[3] *Ibid.* 632.

[4] *Ibid.* 1879, **87**, 578.

[5] *Ibid.* 645.

The use of the spectroscope in studying the earths requires great care, and sometimes the presence of a very minute quantity of some foreign substance may lead to wrong conclusions. Thus the presence of traces of uranium caused Sorby to mistake zirconia for a new oxide that he called jargonia, and some similar cause induced Delafontaine[1] to consider that there was a marked difference between the didymium oxides of cerite and samarskite, didymium oxide of cerite being a mixture of different earths. Soret,[2] however, showed that the didymium oxide from samarskite, as furnished him by Marignac, was the same as that from the oxide from cerite. Lecoq de Boisbaudrant came to the same conclusion from the oxide I had furnished him as coming from samarskite. A still more curious fact is that, in some experiments I made in connection with Lecoq de Boisbaudrant, a peculiar treatment of pure didymium oxide by acids so altered the most important absorption ray furnished in the spectrum of that earth as to destroy its characteristics.[3]

Up to the present time the following earths have been found in samarskite. I give the list as made out by Delafontaine, with the exception of mosandrum, which he does not recognize:

Yttria,
Erbia,
Terbia,
Philippia,
Decipia,
Thoria,
Oxide didymium,
Oxide cerium,
Mosandria.

The proportion of each of these earths in the 14 per cent. of earths it is impossible to state. As regards the thoria it is about 0.50 of the mineral. The oxides of cerium and didymium exist only in traces.

The method of separating most of these earths is by fractional precipitation with oxalic acid, or by some alkali as employed by myself. Operating with the ignited nitrate is used in other instances, but in whatever manner the separation is attempted it is attended with difficulty and greatly reduces the quantity of the residuary oxide which is sought for.

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[1] Comptes rendus, 1877, **85**, 634.

[2] *Ibid.* 1878, **86**, 422.

[3] *Ibid.* 1878, **86**.

It is the insoluble precipitate D that furnishes the difficult problem of quantitative analytical chemistry, and several earths of yet undefined character have been more or less perfectly separated. I will give some of my own labors in that direction.

Many interesting results have been worked out by Marignac, of Geneva, and Delafontaine, of Chicago; but the slow, tedious processes that have to be employed will delay those labors very much.

The method by which I made some imperfect operations on the oxalate C is as follows: The powder is dried, ignited and weighed. It has a pale yellow color, and consists of several earthy oxides. It is completely soluble in dilute or strong nitric acid. The solution of it in the acid is evaporated to the consistency of thick syrup, thus driving off nearly all the free acid. To this syrupy mass, before it solidifies,[1] about 50 cc. of a concentrated solution of sulphate of potassium or sodium (lately I have used the sodium salt altogether), and mixed into the mass. It gives at first a clear solution. To this is added three or four grams of small crystals of the sulphates, the whole stirred frequently and allowed to stand for 24 hours. A precipitate soon begins to form, and at the end of the time is quite abundant. It is now thrown into a filter and thoroughly washed with a concentrated solution of potassium or sodium sulphate, but at no time will the filtrates be entirely free from a trace of the insoluble double sulphate. This precipitate is called D. The filtrate is supposed to contain yttria and erbia. To it is added oxalic acid or ammonium oxalate, the precipitated oxalate burnt, redissolved and reprecipitated[2] by the oxalate, then burnt, and after very thorough ignition, weighed. This oxide is then dissolved in dilute sulphuric acid, evaporated carefully to dryness, and heated nearly to red heat, until its weight is constant. This is noted, and from the weight of the oxide and that of its sulphate, the relative proportion of yttria and erbia is estimated by the formula of Bahn and Bunsen:

$$x = 4.9806A - 2.4540B.$$

$x =$ the erbia contained in A; the oxides, which give B, the sulphates.[1] The first precipitate by the sodium sulphate, washed with a solution of the same, is dissolved in hydrochloric acid, and first precipitated as oxalates, then changed into oxides by ignition. It is in this oxide that I searched for mosandrum by repeated precipitation with sodium sulphate and reconversion into oxides, when I obtained an oxide as dark as cerium oxide, dissolved in minute quantity in sodium sulphate and perfectly soluble in very dilute nitric acid, after 30 minutes' contact.

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[1] We are supposed to be operating with one or two grams of the mineral.

[2] This second precipitation is always necessary when we are analysing these earths and the first solution contains potash and soda.

The insoluble double sulphates D precipitated from the solution of the earths may contain any or all of the other cerium oxides and thoria. This is dissolved in water containing a little chlorhydric acid, by the application of heat; the solution is then nearly neutralized by ammonia and precipitated by oxalic acid or oxalate of ammonia, the precipitate is burnt, redissolved in nitric acid and reprecipitated by the oxalate, which is well burnt and weighed.

This was originally supposed to be the cerium group of earths, but when rubbed up with a little water it is completely dissolved[2] in dilute nitric acid (1 acid to 100 water), in from 15 to 30 minutes, showing the absence of cerium oxide, or if present, only to the extent of a mere trace.

To test this fact still farther, I precipitated the earth from its nitric acid solution by caustic soda, adding just enough to make the solution alkaline, then added 3 to 4 grams of caustic soda, and adding water enough to make the mixture 50 cc., it is quite thick from the gelatinous precipitate. A stream of chlorine gas is now passed slowly through the mixture for 2 or 3 hours, in the manner recommended by M. Mosander for separating cerium oxide from its associated earths. But none of the indications of color peculiar to cerium oxide are manifested, but all the oxides are taken into solution except a small quantity of a white gelatinous precipitate. This precipitate was collected on a filter and washed, detached from the filter and dissolved by means of a few drops of sulphuric acid, evaporated to dryness, heated to drive off the excess of acid, and, when dissolved in a little cold water and examined, was found to be thoria.[3] It was afterwards precipitated by ammonium oxalate, burnt and weighed, and represented 0.80 per cent. This is a new and valuable method of separating thoria, which will be treated of in another part of this paper.

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[1] In the use of this method of operation it was supposed that cerium oxide and yttria could be easily separated from each other by the bisulphate of potassium and sodium, and the oxides remaining in solution were yttria and erbia, but more recent research has shown its defective character, and it is no longer adapted to furnish any good method.

[2] This is based on the supposition that there is no other oxide present.

[3] The cold solution when heated was changed into a mass of the delicate silky crystals so remarkably characteristic of thoria.

The fact of the absence of cerium oxide led to a thorough examination of the D precipitate; for the Russian variety of samarskite contains cerium. But to do this I had to make the study upon a much larger quantity of the earths than that obtained from 5 grams of the mineral, which contain only about 4 per cent. of the D oxides, so that what follows is based on the use of ample material obtained from several kilograms of the mineral.

In this large operation I did not use platinum vessels for the first treatment, but lead vessels, the decomposing vessels being of the capacity of four litres, and capable of working more than one kilogram at a time, and the mineral was sufficiently divided by passing it through a wire sieve with ½ mm. meshes (less than 30 minutes being required to prepare a kilogram for the action of the fluorhydric acid). The mineral is placed in the lead capsule and 750 cc. of water poured upon it, then one kilogram of fuming fluorhydric acid is added by degrees, and the mixture stirred with a lead rod until the violence of the action ceases. Then a second kilogram of acid is added and stirred in. The capsule is now placed on a water-bath and heated, with occasional stirring, for two or three hours, when the action is complete, and we proceed as already described with the 5 grams.

When the insoluble fluorides of the earths are obtained I find the following the best way of changing them to oxalates. 250 grams of the dry fluorides rubbed up in a mortar and placed in a platinum capsule, and then 250 cc. of concentrated sulphuric acid are added without water, the mixture stirred and heated over the flame until nearly dry, and after cooling, dissolving in water and uranium oxide farther oxidized by nitric acid. After filtration the whole is diluted to about 5 litres, boiled by a current of steam, nearly neutralized and then precipitated by 225 grams oxalic acid dissolved in one litre of water. The oxalates thus obtained are operated with as already described for the separation of yttria, using either potassium sulphate or sodium sulphate. The latter has certain advantages in large operations. The thoria of the earths is with that part which is difficultly soluble in sodium sulphate.

Separation of Thoria.

The separation of this earth from the others with which it is usually associated is attended with more or less difficulty and uncertainty. These earths are of the cerium group, for the concentrated solution of potassium sulphate precipitates the thoria along with these earths. One of the best methods is considered to be that by sodium hyposulphite, but the use of it did not enable me to decide upon the presence of thoria when I made the examination for my mineralogical paper on the "Columbic acid minerals of the United States,"[1] while the method about to be described makes it easy of detection and quantitative separation; so much so that I am satisfied that by means of it the metal thorium will be found to be more generally diffused than it has been supposed to be.

If thoria be precipitated from a solution of any of its salts by the fixed alkalies, and the gelatinous precipitate added to a little water containing four or five times its weight of caustic potash or soda, and a current of chlorine gas passed through it for any length of time, none of the thoria will be taken into solution; and if the other earths usually associated with thoria be present, the same result will take place as regards the thoria, but all the other earths will be dissolved with the exception of the cerium oxide. These facts have been fully verified by a special set of experiments. The thoria in the samarskite was estimated in this way,[2] and no analytical result could be more satisfactory, sufficient care being taken to pass chlorine gas through the solution long after it is supposed to be saturated. Two or three hours is not too long where ½ to 1 gram of the mixed oxides is operated with.

Separation of the thoria from the mixed earths by ammonia.—When thoria has to be separated from a large quantity of its associate earths, the chlorine method is long, and the insoluble part has to be separated and treated two or three times before complete separation is accomplished. I accomplished this by an excellent method, but one not intended to furnish quantitative results like the chlorine method.

Using, say fifty grams of the earths separated by the potassium or sodium sulphate, dissolve it in nitric acid somewhat diluted, and concentrate over a water-bath, add the contents of the capsule to about three litres of water, boil by a current of steam or otherwise, and, when in a state of ebullition, neutralize by ammonia until only a few flakes remain undissolved; then add by degrees an ammonia solution of known strength and just sufficient to precipitate six or eight grams of the oxides,[1] the solution being made to boil violently during the operation. This ebullition is continued for about five minutes. A bulky gelatinous precipitate will be formed which contains all the thoria and a little of the other oxides. This is thrown on a filter and washed. This takes place very slowly. The gelatinous precipitate is dissolved in a dilute solution of sulphuric acid, evaporated to dryness, excess of acid driven off, redissolved in cold water. By boiling and evaporation it separates in its well-known form, which, when hot, is separated from the mother-liquor. The sulphate of thorium thus obtained is not perfectly pure, but if wanted for chemical investigations it can be purified by the usual method. This separation clearly arises from the fact that the thoria is less basic than the other earths.

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[1] Am. Journal of Science, **13**, May, 1877.

[2] As already described where treating of the absence of cerium oxide in the samarskite.

The filtrate from the gelatinous precipitate is treated with oxalic acid, and the precipitated oxalate dried and ignited, giving a salmon yellow oxide that is further examined by processes to be described. The fact that these earths have only a mere trace of thoria remaining in them is established by the fact that, when one gram of them is treated by the chlorine test for thoria already described, all the oxides are completely dissolved except 4 milligrams. I then recommend this method as one likely to prove useful for the purification of large quantities of the earths containing thoria in small quantity.

The earth from the thoria is of a salmon yellow color, its oxalate burns readily, and all tests were applied to discover lanthanum oxide, and only a very doubtful evidence of its presence was obtained. So that, of the three cerium metals, only didymium oxide remained to look for. A nitric acid solution gave the very well known spectroscopic bands of that metal, but it was impossible to separate it by a chemical process. But by making use of the spectroscope I think I have approximated to the proportion mixed with the oxides in the following manner:

Quantitative Estimate of Didymium Oxide by its Absorption Bands.

Make solutions of the oxide of didymium of known strength, and place the solutions in tubes of uniform diameter. Vials of thin glass

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[1] In the present instance I have calculated the amount on the basis of an atomic weight of the oxides of 116 (O = 16).

1½ cm. diameter were used. Then take the oxides to be tested, dissolving a known quantity of the oxides in a solution of nitric acid, placing in a tube of the same size as those containing the didymium salt of known strength, compare the solution in the tubes before the spectroscope with the different didymium tubes, and it will be soon seen which one of these latter gives bands corresponding in intensity with the didymium bands in the solution of oxides that are tested; and knowing the exact proportions of oxide in the didymium tube, a good approximate result may be obtained.

I am now making an apparatus, using only one solution of didymium and simply varying at pleasure the thickness of the solution. In this way I estimate that the mixed earthy oxides of samarskite contain less than 0.25 of didymium. As regards the principal portion of the earth separated from the yttria, I consider it as an oxide, or oxide of a new earth, for I cannot reconcile my mind to the idea that it is principally terbia. One of the earths present I call mosandrum, and M. Delafontaine has separated two, phillipium and decipium.

Owing to the fact of bodily indisposition I have not been able to continue my researches on these earths.

For the complete quantitative analysis of samarskite, reference is made to labors previously made by myself and others[1], with this difference that in the earthy oxides there is 0.50 per cent. of thoria, and the cerium referred to is not that oxide, but other mixed oxides.

ON THE ACTION OF AROMATIC OXY-ACIDS ON PHENOLS.

By Arthur Michael.

The investigation of the action of alkalis on naturally occurring organic compounds has shown that a considerable number of these bodies undergo in this operation a decomposition into phenols and aromatic oxy-acids. These compounds are distinguished by the greater or less ease with which they undergo this decomposition.

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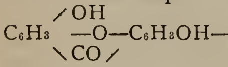
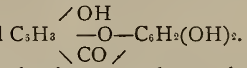
[1] Am. Jour. of Science, May, 1877.

While some of them only require to be heated with dilute aqueous alkaline solutions, others are not decomposed unless they are treated with alkalis at a high temperature. The easily decomposable compounds are probably compound ethers of phenols and oxy-acids; as maclurin, which may be considered the phloroglucinether of protocatechuic acid; or phloretin, the phloroglucinether of phloretic acid. The second class consists largely of compounds which are more or less complicated derivatives of aromatic oxyketones. As examples of this class may be mentioned euxanthone—



$C_6H_3\begin{array}{l}\diagup OH\\ \quad -O-C_6H_3OH\\ \diagdown CO\diagup\end{array}$

—or gentianin, which is probably a methyl-ether of the compound



$C_3H_3\begin{array}{l}\diagup OH\\ \quad -O-C_6H_2(OH)_2.\\ \diagdown CO\diagup\end{array}$

Several compounds showing an analogous behavior towards alkalis have been obtained synthetically. Paradioxydiphenylketone — $C_6H_4<^{OH}_{CO}-C_6H_4OH$—is formed (1) By the action of water at a high temperature on rosaniline[1] or aurine;[2] (2) By the action of potassium hydrate on phenol-phthalein;[3] (3) From diphenylketone by means of the α-dinitro and diamido derivatives.[4] An isomeride, yielding also phenol and p-oxybenzoic acid on fluxing, was obtained in a similar manner from β-dinitrodiphenylketone.[4] The compound $C_6H_4<^{O}_{CO}>C_6H_4$, which may be considered as an ether of the unknown diortho dioxydiphenylketone, has been obtained in the following reactions: by the oxidation of $C_6H_4<^{O}_{CH_2}>C_6H_4$;[5] by the action of phosphorus oxychloride on disodiumsalicylate;[6] among the products obtained by the distillation of o-chlorobenzoic acid, or a mixture of phenylphosphate and sodiumsalicylate;[6] by passing phenol over heated lead oxide,[7] and finally by the oxidation of the compound obtained by heating euxanthone with zinc dust.[8] An analogous compound has been obtained by Buchka by the action of potassium hydrate on gallein.[9]

The present investigation was undertaken in the hope of obtaining some of the natural products synthetically. The results

[1] Liebermann, Ber. 1872, 951, 1878, 1435.

[2] Caro and Graebe, *Ibid.* 1878, 1348.

[3] Baeyer and Burkhardt, Annalen, **202**, 126.

[4] Staedel and Sauer, Ber. 1878, 1747.

[5] Merz and Weith, Ber. 1881, 191.

[6] Richter, J. pr. Chem. [2] **23**, 349.

[7] Behr and Dorp, Ber, 1874, 398.

[8] Wichelhaus and Salzmann, Ber. 1877, 1397.

[9] Annalen, **209**, 270.

described in the present paper will prove that by the direct action of aromatic oxy-acids on phenols, or by the aid of suitable dehydrating agents on such mixtures, bodies belonging to the above class of compounds may be obtained.

Action of Tin tetrachloride on a mixture of Phenol and Salicylic Acid.

A mixture of phenol and salicylic acid was heated both in open vessels and in sealed tubes at various temperatures, without any reaction ensuing. The addition of dehydrating agents to the mixture effects a reaction in an open vessel at a moderate temperature. Zinc chloride and tin tetrachloride have been used, the latter reagent giving the most satisfactory results. The following proportions were found to give the best yield: To 50 grams of phenol and an equal weight of salicylic acid 40 grams of tin tetrachloride were added, and the mixture heated in an oil-bath for twelve to fourteen hours at 115°–120°, finally for several hours at 125°. The salicylic acid soon dissolved in the mixture of phenol and tin tetrachloride, forming at first a colorless liquid which on further heating took a yellow color, growing in intensity of color as the reaction proceeded. After heating several hours, beautiful yellow needles were deposited from the liquid, and continued to separate until the reaction ceased. The melted flux was then poured into a large quantity of boiling water, and the insoluble residue treated with steam to free it from undecomposed phenol. The crystalline product was dissolved in warm alcohol, and the solution treated with hydrogen sulphide to free it from tin. The filtrate, after being concentrated by evaporation, yielded crystals, which were purified by treatment with bone-black and repeated crystallization from alcohol. This method of purification was later given up for the following more simple treatment. The flux, which contains a double compound of the new body with tin tetrachloride, phenol and salicylic acid, was freed from phenol by treating with steam, and the residue boiled with a large excess of a concentrated solution of sodium carbonate. The filtrate, which was found to contain no tin, was treated with carbon dioxide until complete precipitation ensued. The precipitate was dissolved in sodium hydrate, and again treated with carbon dioxide. Towards the end of the precipitation it was noticed that long white needles were deposited in place of a reddish crystalline powder. At this point the originally dark liquid had become light brown, the product was filtered, and the filtrate then treated with carbon dioxide until complete precipitation took place. The red precipitate contained a small quantity of the white needles; these were separated by extracting several times with a small amount of boiling water. The residue was obtained in a pure state by two crystallizations from benzene and one from alcohol, after treatment with animal charcoal.

Zinc chloride, in place of tin tetrachloride as dehydrating agent, gave a very small yield of the new substance. A mixture of equal weights of phenol, salicylic acid and fused powdered zinc chloride formed on heating a homogeneous liquid, which soon took a dark yellow color. The mixture was heated for six hours, and the flux then treated with sodium carbonate and carbon dioxide as above described.

An analysis of the substance gave the following numbers : 0.2466 gram, dried at 100°, gave 0.6596 gram of CO_2 and 0.1085 gram of H_2O.

	Theory for $C_{13}H_{10}O_3$.	Found.
C	72.89	72.91
H	4.67	4.88
O	22.44	22.21

The hot aqueous solution of the substance deposits, on cooling, large, glittering, pale-yellow plates; the hot alcoholic solution, small well-defined plates. A solution in benzene, saturated at its boiling point, yields on cooling pyramids with symmetrically truncated end-faces. The substance melts at 143–144°. It is almost insoluble in cold, moderately soluble in hot water. Alcohol and benzene dissolve it readily in the hot, sparingly in the cold. Alkalis dissolve it with ease in the cold to form the corresponding phenylate. This solution treated with carbonic acid yields a precipitate of the original compound. In the preparation of the substance attention was called to the separation of yellow needles from the melted flux. These needles are a double compound of the substance with tin tetrachloride, and are obtained when the two substances are brought together. They are readily soluble in water and alcohol. The analysis and investigation of the properties of the compound show that it is a dioxybenzophenone. To distinguish it from the isomeric paradioxybenzophenone I propose the name salicylphenol.[1] The substance is formed by the elimination of a molecule of water from a molecule of salicylic acid and one of phenol, a reaction represented by the equation:

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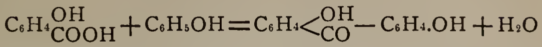
[1] The unknown phenolether of salicylic acid should be called phenylsalicylate or salicylphenolether.



$$C_6H_4\begin{matrix}OH\\COOH\end{matrix} + C_6H_5OH = C_6H_4<\begin{matrix}OH\\CO\end{matrix} - C_6H_4.OH + H_2O$$

Salicylphenol forms a series of well-defined derivatives, in which the hydrogen of the hydroxyl groups are replaced by metals. To obtain the sodium derivative an excess of the powdered substance was allowed to stand with dilute aqueous sodium hydrate for several days, and the undissolved substance separated by filtration. The filtrate evaporated to incipient dryness solidified to stellular groups of navicular-shaped needles, which are very soluble in water and alcohol.

0.4580 gram Na compound, dried at 100°, gave 0.2486 gram Na_2SO_4.

	Theory for $C_6H_4\begin{matrix}ONa\\CO\end{matrix}C_6H_4ONa$.	Found.
Na_2	17.83	17.60

The silver compound was obtained as a bright yellow precipitate by addition of silver nitrate to an aqueous solution of the sodium derivative. It is sparingly soluble in water, and contains one molecule of water of crystallization.

0.6904 gram silver compound, air-dried, lost 0.0272 gram H_2O when dried at 100°.

	Theory.	Found.
H_2O	4.01	3.79

I. 0.4483 gram Ag compound, dried at 100°, gave 0.206 gram Ag.

II. 0.3863 gram Ag compound, dried at 100°, gave 0.179 gram Ag.

	Theory for $C_6H_4\begin{matrix}OAg\\CO\end{matrix}C_6H_4OAg$.	Found. I.	 II.
Ag_2	46.55	46.00	46.33

The mercuric salt separated on addition of a solution of mercury dichloride to an aqueous solution of disodiumsalicylphenylate as a reddish yellow precipitate. It is sparingly soluble in hot water, and is deposited from this solution on cooling as navicular-shaped needles. When it is boiled with a small quantity of water the color of the salt changes to red. The addition of iron trichloride to a solution of the sodium derivative gave a brown precipitate.

This is moderately soluble in water, and is deposited from the hot aqueous solution on cooling as fern-shaped crystals.

The copper derivative formed a greenish-yellow precipitate, and is insoluble in hot water. By boiling with water the amorphous precipitate changed into crystalline groups of rhombic plates.

A lead derivative was obtained as a yellow amorphous precipitate, which melted under boiling water. The aqueous solution of disodiumsalicylphenylate was not precipitated by addition of barium nor calcium chlorides.

The second substance formed by the action of tin tetrachloride on salicylic acid and phenol is obtained by precipitating the filtrate from salicylphenol with carbonic or hydrochloric acid. The substance was purified by repeated crystallization from water. An analysis proved that the substance has the same empirical formula as salicylphenol. 0.2071 gram substance, dried at 100°, gave 0.5516 gram CO_2 and 0.930 gram of H_2O.

	Theory for $C_{13}H_{10}O_3$.	Found.
C	72.89	72.68
H	4.67	4.97

The substance separates from hot water, in which it is more soluble than salicylphenol, in plates or needles, from alcohol in large plates. It melts at 205.5°–206.5°. Boiled with acetic anhydride and sodium acetate it yields an acetyl derivative. This crystallizes in long needles, melting at 148°. A comparison of these properties with those of paradioxybenzophenone[1] shows that the compounds are identical. The formation of this compound was due to the presence of a small amount of paraoxybenzoic acid in the commercial salicylic acid used.[2] This view was confirmed by the direct synthesis of paradioxybenzophenone from paraoxybenzoic acid and phenol. These substances heated with tin tetrachloride for ten hours, and the product treated as described for the preparation of salicylphenol, yielded paradioxybenzophenone.

Action of Acetic-anhydride on Salicylphenol.

Acetic anhydride converts salicylphenol readily into the diacetyl derivative. A mixture in the proportion of one mol. salicylphenol, three mols. acetic anhydride, and one mol. fused sodium acetate was heated for several hours in boiling water. The product was poured in cold water. The insoluble oil soon solidified to a crystalline mass, which was purified by several crystallizations from dilute alcohol.

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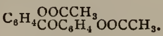
[1] Staedel and Gail, Annalen, **194**, 334. Baeyer and Burkhardt, *Ibid.* **202**, 129.

[2] Ost, Journ. p. Chem. [2] **20**, 208.

An analysis of the substance, dried in vacuum over H_2SO_4, gave the following numbers:

0.2150 gram substance gave 0.5417 gram CO_2 and 0.0965 gram H_2O.



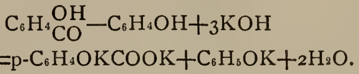
	Theory for $C_6H_4\begin{smallmatrix}OOCCH_3\\COC_6H_4OOCCH_3.\end{smallmatrix}$	Found.
C	68.47	68.71
H	4.69	4.98

Diacetsalicylphenol separates from hot water in long, concentrically grouped white needles, that melt at 84°–85°. They are sparingly soluble in cold, moderately soluble in hot water. In cold alcohol and benzene moderately soluble, they are readily soluble in these solvents when warm. An aqueous solution of potassium hydrate does not dissolve the compound in the cold; when heated it is gradually dissolved, forming a yellow solution. Carbonic acid precipitated salicylphenol from this solution.

Action of Potassium and Sodium Hydrates on Salicylphenol.

The formation of salicylphenol from salicylic acid shows that the relation of one of the hydroxyl groups to the carbonyl group is that of ortho-derivatives. The products obtained by fluxing salicylphenol with alkalis make it probable that the relation of the second hydroxyl group is that of para-derivatives.

Salicylphenol was heated with three times its weight of potassium hydrate and a small quantity of water until the addition of hydrochloric acid to a portion of the flux dissolved in water ceased to give a precipitate. The yellow color of the flux gradually changed to a light brown. The flux was dissolved in water, acidified with dilute sulphuric acid, filtered, and the filtrate treated with steam. The distillate contained phenol. This was shown by isolation of the product and comparison of its properties with those of phenol. Tribromphenol (melting point 97°) was immediately precipitated on addition of bromine to the distillate. The liquid remaining in the flask after treatment with steam was extracted several times with ether, and the extracts evaporated to dryness. The white crystalline substance which remained was crystallized several times from water, and then showed all the properties of paraoxybenzoic acid. The fact that a number of ortho-benzene derivatives have been shown to pass over into para-compounds by fluxing with potassium hydrate made it desirable that the experiment should be repeated, using sodium instead of potassium hydrate. The experiment showed that the same products are formed in the action of sodium hydrate on salicylphenol. Salicylphenol is therefore an ortho-para derivative of benzophenone. The action of alkalis is represented by the equation:



$$C_6H_4\overset{OH}{\underset{CO}{}}—C_6H_4OH+3KOH$$
$$=p\text{-}C_6H_4OKCOOK+C_6H_5OK+2H_2O.$$

The decomposition of orthoparadioxybenzophenone into paraoxybenzoic acid and phenol is of interest as showing the effect of the hydroxyl groups upon the affinity of the carbonyl group to the phenylene radical. It indicates that the ortho-hydroxyl group loosens the affinity to a greater extent than the para-hydroxyl group.

Action of nascent Hydrogen on Salicylphenol.

The carbonyl group of salicylphenol is not reduced by subjecting the compound to the action of zinc and hydrochloric acid or potassium hydrate and zinc dust. The reduction may be easily effected by allowing sodium amalgam to act on an alkaline solution of the substance. Sodium amalgam (2 per cent. Na) was gradually added to a solution of salicylphenol in potassium hydrate, and the reaction continued until the liquid became perfectly colorless. The alkaline liquid was then decanted from the mercury, and carbon dioxide passed through it until complete precipitation of the reduction product. All attempts to obtain the white amorphous precipitate in a crystalline form were without success. For purification it was dissolved in potassium hydrate, and again precipitated by treatment with carbon dioxide.

An analysis of the substance, dried over sulphuric acid *in vacuo*, gave the following numbers:

0.2017 gram substance gave 0.5323 gram CO_2 and 0.0987 gram H_2O.

	Theory for $C_{13}H_{12}O_3$.	Found.
C	72.89	72.68
H	4.67	4.97

The compound was formed by the addition of two hydrogen atoms to salicylphenol, and is o-p-dioxydiphenylcarbinol:

$$C_6H_4OHCOC_6H_4OH+H_2=C_6H_4OHCHOHC_6H_4OH.$$

Dioxydiphenylcarbinol is a white amorphous powder, which, when rubbed with an insulator, becomes strongly electric. It is insoluble in cold, somewhat soluble in hot water. Heated with a small quantity of boiling water the substance melts. Cold alcohol dissolves it readily; the alcoholic solution leaves an oil on evaporation of the alcohol which did not solidify on standing. In alkalis it is readily soluble, forming the corresponding phenylates. O-p-dioxydiphenylcarbinol, like diparadioxydiphenylcarbinol,[1] undergoes a very striking change when heated with mineral acids. It is converted into a dark violet-blue color. The reaction is extremely delicate; several drops of dilute hydrochloric acid suffice to convert a considerable quantity of the carbinol into the blue color. Neither the color nor its acetyl derivative could be obtained in a crystalline state. Distilled over zinc dust in a current of hydrogen it gave a small yield of a crystalline substance.

Action of Salicylic Acid on Resorcin.

While the formation of salicylphenol takes place only when salicylic acid and phenol are heated in presence of a dehydrating agent, it was found that an oxyketone was formed by heating a mixture of salicylic acid and resorcin, and that the same mixture heated with a dehydrating agent gave a different result.

To investigate the action of salicylic acid on resorcin, a mixture of 8 parts of the acid and 15 parts of resorcin was put in a long-necked flask, and heated in an oil-bath at 195°–200° for about 15 hours. It is advisable to keep the temperature of the bath at 195° for the first five hours, and then to raise it to 200°. The mixture soon took a dark brown color, a sublimate of salicylic acid was formed and the deposition of water and phenol took place on the sides of the flask. The hot flux, which becomes quite hard on cooling, was poured into cold water slightly acidulated with hydrochloric acid, and allowed to stand for 12 hours. The insoluble crystalline residue was extracted with a dilute solution of sodium carbonate—a saturated solution of the salt diluted with six parts of water—which dissolves a brown amorphous substance and undecomposed salicylic acid. The brown-yellow residue was dissolved in alcohol, boiled several hours with animal charcoal, some water added to the filtrate and the solution boiled until it became turbid. On cooling, part of the substance separated as an oil, which solidified on cooling; the greater part crystallized out as large yellowish-red scales after the solution had cooled. To obtain the substance pure it was extracted with ligroin containing a small amount of chloroform, which left a slight impurity undissolved, and crystallized twice from this solvent.

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[1] Baeyer and Burkhardt, Annalen **202**, 132.

On analysis the substance gave the following numbers:

0.2623 gram of substance gave 0.6522 gram of CO_2 and 0.1085 gram of H_2O.

	Theory for $C_{13}H_{10}O_4$.	Found.
C	67.82	67.79
H	4.35	4.59

From hot dilute alcohol it is deposited on cooling as glistening yellow scales; from ligroin as arborescent, pale yellow, crystalline groups. It is insoluble in cold, very slightly soluble in hot water. Alcohol and benzene dissolve it readily. Treated with alkalis in the cold it dissolves to form a yellow solution. A dilute solution of potassium carbonate dissolves it slowly. From these solutions carbonic acid precipitates the original substance. Heated with water it volatilizes slowly, giving the steam a peculiar aromatic odor. The crystals melt at 133–134°; the melted substance solidifies at 116–117°. Acetic anhydride converts the compound into an acetyl derivative. This formed an oil, which solidified partially after long standing, but the solid compound was not obtained in sufficiently pure state for analysis. A solution of the substance in concentrated aqueous potassium hydrate may be boiled without decomposing the ketone. It is easily decomposed when fluxed with alkalis. Heated with caustic potash and a small amount of water for several minutes, the presence of salicylic acid and resorcin was proved in the flux by their isolation. An alkaline solution of the substance treated with sodium amalgam gave a product with properties similar to those of dioxydiphenylcarbinol. The white reduction product gave a green coloring matter when heated with dilute acids.

The above described properties of the substance show that it is a trioxybenzophenone or salicylresorcin. This view is corroborated by its behavior towards zinc chloride, which will be described further on. The yield of salicylresorcin obtained in the above process was very small.

$$C_6H_4OHCOOH + C_6H_4(OH)_2$$
$$= C_6H_4(OH)COC_6H_3(OH)_2 + H_2O.$$

Action of Zinc Chloride on a mixture of Resorcin and Salicylic Acid.

It has already been mentioned that the action of salicylic acid on resorcin, in the presence of zinc chloride, gives rise to a new product. The following directions were found to give the best result, although the yield obtained was but small. Twenty grams of resorcin and an equal weight of salicylic acid were melted, and about fifteen grams of fused, pulverized zinc chloride added to the clear flux. The flux soon took a yellow, then a yellowish-brown color, which increased in intensity with continued heating. After the mixture had been kept melted for about two hours, it was poured into ¼ liter of warm water. The dark residue may be purified by crystallizing once from glacial acetic acid and then three times from alcohol. A more advantageous method of purification is founded on the insolubility of the sodium derivative of the new compound. The flux, after treatment with warm water, was extracted several times in the cold with an aqueous solution of dilute sodium hydrate. The straw-colored residue was then treated with hydrochloric acid, filtered, and the insoluble portion crystallized twice from alcohol.

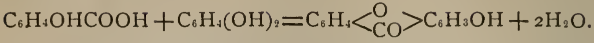
The substance does not contain water of crystallization.

0.356 gram of air-dried substance weighed 0.355 gram when dried at 100°.

0.261 gram of substance, dried at 100°, gave 0.7051 gram of CO_2 and 0.0872 gram of H_2O:

	Theory for $C_{13}H_8O_3$.	Found.
C	73.58	73.68
H	3.77	3.71

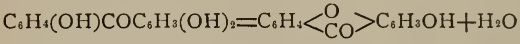
The formula $C_{13}H_8O_3$ is that of salicylresorcin less one molecule of water. That the new compound stands in the relation of that of an anhydride to salicylresorcin will be shown below. I propose the name salicylresorcin ether, as indicating this relationship. Its formation from salicylic acid and resorcin may be represented as follows:



$$C_6H_4OHCOOH + C_6H_4(OH)_2 = C_6H_4 < \substack{O \\ CO} > C_6H_3OH + 2H_2O.$$

Salicylresorcin ether crystallizes from alcohol in long, bright yellow needles. It is insoluble in cold, but sparingly in hot water. Cold alkaline solutions convert it into yellow, slightly soluble needles, consisting of the corresponding phenylate. It melts at 146–147°.

Salicylresorcin ether can be obtained from salicylresorcin by the action of zinc chloride. The latter substance and an equal weight of zinc chloride were kept melted for about ten minutes. The flux was treated in the same manner as the flux obtained in the preparation of salicylresorcin ether and yielded this compound:



$$C_6H_4(OH)COC_6H_3(OH)_2 = C_6H_4 < \substack{O \\ CO} > C_6H_3OH + H_2O$$

The inverse reaction, to obtain salicylresorcin from its ether, was not realized. Fused with sodium and potassium hydrates it gave the same decomposition products as salicylresorcin, *i. e.* salicylic acid and resorcin.

Salicylresorcin ether forms a series of metallic derivatives, characterized by their insolubility in water. This property is even shown by the alkali derivatives, which are among the least soluble products containing these metals. Only the sodium derivatives have been examined, but the results already obtained will be found to present some interest.

A boiling saturated solution of salicylresorcin ether (one mol.) poured into a solution of sodiumethyloxide (three mol.) in 80 per cent. alcohol gave momentarily a clear yellow solution. This soon solidified to a mass of lemon-colored, long needles, which were washed with a small quantity of absolute alcohol, then well pressed between bibulous paper and dried at 110°. On analysis the following results were obtained:

I. 0.4990 gram of substance, dried at 110°, gave 0.2555 gram of Na_2SO_4.

II. 0.2945 gram of substance, dried at 110°, gave 0.1556 gram of Na_2SO_4.

	Theory for $C_{13}O_3H_7Na, NaOH$	Found.	
		I.	II.
Na	16.76	16.57	17.10

This disodium derivative treated with water, or a large amount of alcohol, gives products containing less sodium; a substance having a constant composition could not be obtained. It was found that by repeated treatment with cold water the complete decomposition of the disodium compound into salicylresorcin ether and sodium hydrate could be effected. The disodium compound is stable in the presence of strong aqueous or alcoholic sodium hydrate. An alcoholic solution of the ether poured into an excess of aqueous sodium hydrate gave a precipitate of pale yellow needles. This consisted largely of the mono-sodium derivative, as the following analysis showed:

0.4568 gram of substance, dried at 100°, gave 0.1653 gram of Na_2SO_4.

	Theory for $C_{13}O_3H_7Na$.	Found.
Na	9.83	11.72

Salicylresorcin ether treated with potassium and ammonium hydrates gave derivatives with properties similar to those of the disodium compound.

Relative to the constitution of the disodium compound it might be supposed that salicylresorcin ether adds sodium hydrate, forming $C_6H_4{<}^{ONa}_{CO}{-}C_6H_3{}^{OH}_{ONa}$, a derivative of salicylresorcin. This view cannot be upheld, as salicylresorcin is readily soluble in sodium hydrate, and no precipitate is formed by the addition of a large excess of that reagent to the solution. The fact that the disodium compound when treated with acids yields the ether, while salicylresorcin can only be converted into the ether by means of a strong dehydrating agent, also shows it to be a derivative of the ether. It is not unlikely that the carbonyl group of the ether plays a part in the formation of the disodium compound. There are facts known which seem to imply the capability of the carbonyl group in certain cases of uniting with the alkaline hydrates to form derivatives of the types $\left(=C^{OM}_{OH}\right)$ and $=C^{OM}_{OM}$.[1] From this point of view the

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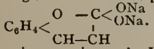
[1] The metallic derivatives of coumarin (Williamson, Chem. Soc. Jour. **28**, 850) probably belong to this class of compounds. The disodium compound would have the constitution



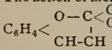
$C_6H_4{<}\begin{matrix}O & -C{<}^{ONa}_{ONa} \\ CH & -CH\end{matrix}$. These compounds have lately been made the subject of some interesting experiments by W. H. Perkin (Chem. Soc. Jour. 1877, 388; 1881, 409 and 554). This chemist obtained by treating equal molecules of the disodium compound and methyliodide the sodium salt of an acid, which is isomeric with the methylcumaric acid obtained by the action constitution of disodium salicylether may be represented by the formula $C_6H_4<\begin{smallmatrix}O\\COH\\ONa\end{smallmatrix}>C_6H_4ONa$. The action of methyliodide on the sodium compound yields methyl substitution derivatives, the examination of which will probably help to a better understanding of the constitution of this class of compounds.

Action of Acetic Anhydride on Salicylresorcin-ether.

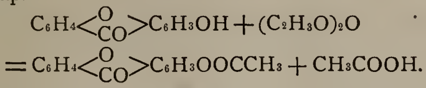
To prepare the acetyl derivative of salicylresorcin ether, equal parts of this substance and fused sodium acetate, and three parts of acetic anhydride were heated for three hours at 110°. The contents of the flask poured into cold water yielded an oil, which soon solidified. The crystalline mass was crystallized several times from alcohol. It separates from hot alcohol as white, prismatic needles, which melt at 167°-168°. The crystals are very slightly soluble in cold or hot water; easily in hot, sparingly in cold alcohol. Heated

of methylsalicylaldehyde on acetic anhydride. It was also noticed that the first acid (α-acid) goes over on heating into the second acid (β-acid), and that this property extends to the ethers of the α-acid. A comparison of the physical properties of the corresponding derivatives of the two acids showed that the boiling points, densities and magnetic rotary power of the α-derivatives are lower than those of the β-series. For these facts, and that "this isomerism cannot be explained by any ordinary kind of chemical constitutional formula we have at present," Perkin offers the following explanation:

"These facts would seem to indicate that in the α-compounds the groups, or some of them, contained in the molecules are farther apart than in the β-compounds."

It does not seem to me that our knowledge of this interesting case of isomerism has been at all increased by this hypothesis. To take an illustration, let us suppose that the conversion of methylaniline chlorhydrate into toluidine chlorhydrate by heat had been discovered when their isomerism could not be explained by "any ordinary kind of chemical constitutional formula," and it was known that p-toluidine has a higher boiling point and greater density than methylaniline, would the hypothesis that the "groups, or some of them," in the molecule of methylaniline are farther apart than in p-toluidine have been a satisfactory explanation? If I rightly understand what Perkin means by "any ordinary kind of chemical constitutional formula," I think this chemist will find that the isomerism of the α and β-acids may be easily represented by constitutional formulæ. The action of methyliodide on disodium coumarin gives the sodium derivative of , a compound which is a lactone derivative of mono-methylorthocoumaric acid, and is isomeric with $C_6H_4<\begin{smallmatrix}O-CH_3\\CH-CH-COOH\end{smallmatrix}$. The acid ethers of the ortho-organic acids are as yet but little known. There is however a class of compounds discovered by Nencki and Sieber (Journ. pkt. Chem. [2], **23**, 147), which undoubtedly belong to this group. Thus the compound obtained by the action of zinc chloride on acetic acid and resorcin should have the formula $C_6H_4<\begin{smallmatrix}O\\O\end{smallmatrix}>C(OH)-CH_3$, and is the acid resorcin ether of ortho-acetic acid or metaphenyleneorthoacetate. This view is in accordance with the properties of the compound, whereas the formula given by the discoverers $C_6H_3\begin{smallmatrix}(OH)_2\\CO.CH_3\end{smallmatrix}$—is in direct opposition to the compound yielding only a monoacetyl derivative, and its decomposition into resorcin and sodium acetate by boiling with aqueous sodium hydrate.

with an aqueous solution of sodium hydrate, sodium acetate and the yellow sodium derivative of salicylresorcin ether are formed. The analysis shows that salicylresorcin ether contains one hydroxyl group.



$$C_6H_4{<}^{O}_{CO}{>}C_6H_3OH + (C_2H_3O)_2O$$
$$= C_6H_4{<}^{O}_{CO}{>}C_6H_3OOCCH_3 + CH_3COOH.$$

0.2326 gram of substance, dried at 100°, gave 0.6063 gram of CO_2 and 0.0882 gram of H_2O.

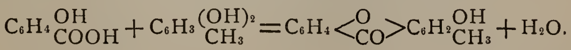
	Theory for $C_{13}H_7O_3(C_7H_3O)$.	Found.
C	70.86	71.08
H	3.82	4.21

Action of Zinc Chloride on Salicylic Acid and Orcin.

A mixture of ten grams of orcin and 10 grams of salicylic acid was melted and 8 grams of powdered zinc chloride gradually added. The flux soon became yellow, and gradually changed to a dark brown color. After heating two hours, at a temperature sufficient to keep it in a melted state, the flux was poured into hot water, boiled out for several minutes and filtered. The dark residue was extracted several times with a solution of sodium carbonate, filtered, and the insoluble part crystallized three times from hot alcohol. The analysis gave the following numbers: 0.2136 gram of substance, dried at 100°, gave 0.5861 gram of CO_2 and 0.0900 gram of H_2O.

	Theory for $C_{14}H_{10}O_3$.	Found.
C	74.34	74.75
H	4.42	4.72

The substance crystallizes from hot alcohol as straw-colored, silky needles, melting at 140°. They are insoluble in cold and hot water; sparingly soluble in cold, more easily in hot alcohol. With alkalis they combine to form metallic derivatives, which are somewhat more soluble in water than the corresponding derivatives of salicylresorcin ether. Fluxed with caustic potash they are decomposed into salicylic acid and orcin. About three grams of the substance were obtained by using 10 grams orcin. It may be called salicylorcin ether or methyloxybenzophenone oxide.



$$C_6H_4{}^{OH}_{COOH} + C_6H_3{}^{(OH)_2}_{CH_3} = C_6H_4{<}^{O}_{CO}{>}C_6H_2{}^{OH}_{CH_3} + H_2O.$$

Only the sodium derivatives of salicylorcin ether have been examined. A boiling alcoholic solution of the substance was poured into an excess of strong aqueous caustic soda. In a few moments long yellow needles separated from the solution. These were filtered, washed with alcohol and dried on the air. They contain water of crystallization, which is not completely given off until they are heated to 125°.

I. 0.5412 gram of substance, air-dried, heated to 125°, lost 0.0520 gram of H_2O.

II. 0.5345 gram of substance, air-dried, heated to 125°, lost 0.0495 gram of H_2O.

0.6870 gram of substance, dried at 125°, gave 0.2047 gram of Na_2SO_4.

	Theory for $C_{14}O_3H_9Na$.	Found. I.	Found. II.
Na	9.28	9.63	
$1\frac{1}{2}H_2O$	9.45	9.60	9.24

A compound corresponding to the disodium salicylresorcin ether was not obtained. The analyses of the sodium derivative, obtained in a manner as already described for the resorcin compound, gave sodium percentages between those of the mono- and di-sodium compounds.

I. 0.6440 gram of substance, dried at 105°, gave 0.2555 gram of Na_2SO_4.

II. 0.6993 gram of substance, dried at 120°, gave 0.2813 gram of Na_2SO_4.

	Theory for $C_{14}O_3H_9Na,NaOH$.	Found. I.	Found. II.
Na_2	15.93	12.85	13.03

Action of Acetic Anhydride on Salicylorcin-ether.

Equal parts of the orcin compound and fused sodium acetate were heated with four parts of acetic anhydride for three hours in a salt-water bath. The product of the reaction brought into cold water, solidified on standing to a white, crystalline mass, which was purified by three crystallizations from hot alcohol. The analysis gave the following numbers:

0.2300 gram of substance, dried at 100°, gave 0.6030 gram of CO_2 and 0.0930 gram of H_2O.

	Theory for $C_{14}H_9O_3(C_2H_3O)$.	Found.
C	71.64	71.50
H	5.47	4.49

From hot alcohol it is deposited on cooling as long white needles, resembling those of o-phthalic anhydride as obtained by sublimation. They are insoluble in hot water; easily soluble in hot, sparingly in cold alcohol. They melt at 151°-152°. Heated with an aqueous solution of caustic soda, the yellow sodium salicylresorcin ether and sodium acetate are formed.

Salicylresorcin ether and salicylorcin ether belong very probably to the same class of compounds as euxanthone and gentianin. With a view of obtaining these products the action of dehydrating agents on mixtures of oxysalicylic acid and resorcin, and methoxysalicylic acid and phlorglucin, will be next examined.

TUFTS COLLEGE, MASS., *April 4th*, 1883.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.

BY W. A. NOYES.

It is well known that in many benzene derivatives, where a methyl group is protected from oxidation by chromic acid by the presence of a negative atom or group, the same methyl may be readily oxidized by potassium permanganate in alkaline solution. The question arises, Is this difference of action due to the fact that one oxidizing agent is acid while the other is alkaline, or is it due to the particular character of each agent? That some, at least, have thought the former to be true seems to be evident from the statement which Richard Meyer has recently given of Remsen's law: "Negative Atome oder Atomgruppen, welche sich in der Orthostellung gegen Kohlenwasserstoffreste im Benzolkern befinden, üben einen schützenden Einfluss auf diese Reste aus, wenn die Verbindungen mit sauren Oxydationsmitteln behandelt werden, Wirkt dagegen ein alkalisches Oxydationsmittel ein, so wird gerade umgekehrt der in Orthostellung befindliche Rest oxydirt."[1] The first paragraph in this statement of the law is almost exactly in Remsen's own words,[2] although the statement first given in this Journal[3] is more carefully worded and less general.

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[1] Aromatische Verbindungen, p. 179.

[2] Remsen, Berichte der deutschen chemischen Gesellschaft, **11**, 2091.

[3] **1**, 36.

Up to the time when the experiments described in this paper were undertaken, the only acid oxidizing agents which had been studied in such a way as to yield results of value as bearing on the question here stated were chromic acid and nitric acid; and the alkaline agents were caustic potash and potassium permanganate. The action of chromic acid has been so fully discussed in this Journal that it requires only to be mentioned here. With this agent, very few exceptions to the protective action of ortho negative atoms or groups are known, and most of these occur where the group to be protected is large or unsaturated.

The action of nitric acid has been far less exhaustively studied than that of chromic acid. Enough, however, is known to show that no such general law holds for nitric acid as for chromic acid, since ortho-toluene derivatives may be oxidized to substituted benzoic acids by the former.[1] Yet, in the case of mesitylene and cymene-derivatives, methyl groups have, in a number of cases, been shown to be protected from oxidation with nitric acid by the presence of ortho negative atoms or groups.[2] But, when the negative atom or group is not present, only one of the hydrocarbon residues is oxidized by nitric acid, so that the negative atom seems rather to determine which group shall remain intact, than to exert a strong protective action.

Of the alkaline oxidizing agents, caustic potash has been used almost exclusively in oxidizing phenol derivatives. On the basis of Jacobsen's experiments, Remsen[3] has shown that in these compounds caustic potash oxidizes most readily the methyl group which is ortho to the hydroxyl group.

The only alkaline agent which has been used in oxidizing derivatives of the same nature as those which have been studied so extensively with reference to the action of chromic acid, is potassium permanganate. This readily oxidizes methyl which is ortho to a negative atom or group. The cases of ortho-toluene derivatives thus oxidized are so numerous and so well known as not to require enumeration here. As regards substitution products containing more than one oxidizable residue, one of the most interesting cases is that of sulpho-cymene. R. Meyer and A. Baur[4] have shown that this compound potassium permanganate oxidizes the methyl group which is ortho to the sulphonic group *first*, in marked contrast to nitric acid which oxidizes only the propyl group. Remsen, who has repeatedly made use of this agent in studying the trisubstitution products of benzene, states[1] that where two groups are to be oxidized, the oxidation is best effected in two stages, the meta or para group with reference to a negative atom or group being first oxidized with chromic acid and afterwards the ortho methyl being oxidized with potassium permanganate.

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[1] Kekulé, Berichte der deutschen chemischen Gesellschaft, **7**, 1007; Zincke, *Ibid.* 1502.

[2] Fittig and Storer, Annalen der Chemie, **147**, 8; Kelbe, Berichte, etc., **15**, 41; Landolph, Berichte, etc., **5**, 268.

[3] Berichte der deutschen chemischen Gesellschaft, **11**, 2091.

[4] *Ibid.* **13**, 1495.

Using the terms ortho, meta and para with reference to the position of hydrocarbon residues toward a negative atom or group, our present knowledge is about as follows: chromic acid either does not oxidize ortho groups at all or oxidizes them in very small amount; nitric acid can oxidize ortho groups, but, where there is a choice, oxidizes meta or para groups by preference; caustic potash has been used only with one class of compounds, but there oxides ortho groups; potassium permanganate in alkaline solution oxidizes ortho, meta and para groups, but, where there is a choice, in some cases at least, it oxidizes ortho groups by preference.

On the whole, then, the general statement of the law as regards acid and alkaline oxidizing agents is justified so far as the agents most frequently used are concerned, although the law in many cases does not hold absolutely. The experiments here described were undertaken for the purpose of determining whether the general statement of the law would hold for another alkaline oxidizing agent. The agent chosen was potassium ferricyanide with caustic potash.

Oxidation of the Nitro-toluenes.

The first substance selected for study was ortho-nitro-toluene. The specimen used in the experiments was procured from Kahlbaum in Berlin. It boiled at 221°–229° (cor.) and, as will be seen later, contained some paro-nitro-toluene.

The proportions used in the oxidation were, 2 grams of potassium ferricyanide, 23 grams of caustic potash, and 200 grams of water. Some experiments were made with a more concentrated solution of the ferricyanide, but the proportions given above were found to work best. The calculated amounts in accordance with the reaction:

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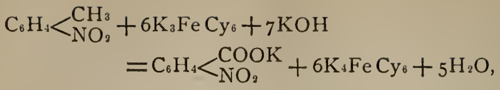
[1] This Journal, 2, 414.



$$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{NO_2}} + \mathrm{6K_3Fe\,Cy_6} + \mathrm{7KOH} = \mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{COOK}}{\mathrm{NO_2}} + \mathrm{6K_4Fe\,Cy_6} + \mathrm{5H_2O},$$

are, 50 grams of potassium ferricyanide, 9.93 grams of caustic potash and 3.47 grams of nitro-toluene.

There were some secondary reactions which led to the evolution of ammonia and the formation of considerable quantities of potassium carbonate and ferric oxide; but, as all of these were formed when the oxidizing mixture was boiled alone, the reactions leading to their formation were not especially studied.

The mixture, as described above, was boiled for two or three hours with an inverted condenser. At the end of this time the ferricyanide was mostly reduced to ferrocyanide, and there always remained some unoxidized nitro-toluene. The latter was distilled off with water-vapor. About two grams of nitro-toluene were recovered from eight grams oxidized in the proportions given above. After the nitro-toluene had been removed, the fluid was filtered from the ferric oxide which always separated, and the filtrate was acidified with hydrochloric acid and extracted with ether. In acidifying it was found best to add only enough acid to a little more than decompose all the carbonates present, since, if a large excess of acid was added, on shaking with ether a great mass of hydroferrocyanic acid was precipitated, which interfered very much with further work. Hydroferrocyanic acid was found to be stronger than any of the substituted benzoic acids worked with, and so there arose no difficulty from there being no free hydrochloric acid in the solution which was to be extracted.

On distilling off the ether a residue remained which proved to be a mixture of two acids. These were separated, partly by the different solubility of the acids in water, and partly by the different solubility of their barium salts.

One barium salt crystallized in thin yellow prisms which were difficultly soluble in cold water. The acid separated from these fused at 240° (cor.) The air-dry salt was analyzed with the following results:

I. 0.2486 gram of the salt lost 0.0396 gram H_2O at 150° and gave 0.1041 gram $BaSO_4$.

II. 0.2397 gram of the salt lost 0.0385 gram H_2O at 150° and gave 0.1015 gram $BaSO_4$.

	Calculated.		Found. I.	Found. II.
$(C_7H_4NO_4)_2$	332	59.39	...	...
Ba	137	24.51	24.62	24.90
$5H_2O$	90	16.10	15.93	16.06

This salt was accordingly that of para-nitro-benzoic acid. It evidently came from para-nitro-toluene which was mixed with the ortho compound.

For the sake of completeness in this part of the work, one gram of para-nitro-toluene (fusing point 53°) was oxidized by boiling for three hours with 25 grams of potassium ferricyanide, 12 grams of caustic potash and 100 grams of water. The filtrate from the ferric oxide was evaporated to a small bulk and, when cold, filtered from the potassium ferrocyanide which crystallized out, and the para-nitro-benzoic acid in the filtrate precipitated with hydrochloric acid. The acid thus obtained fused at 240°–241° (cor.). The analysis of the barium salt gave the following results:

0.3437 gram of the salt lost 0.0552 gram H_2O at 140° and gave 0.1431 gram $BaSO_4$.

	Calculated.	Found.
Ba	24.51	24.48
$5H_2O$	16.10	16.06

The second acid obtained from the oxidation of the mixed nitrotoluene was far more soluble in water. Its barium salt was also very soluble, even in cold water. From a concentrated solution the salt separated in concentrically grouped crystals of an orange yellow color. The acid separated from a portion of these fused at 146° (cor.). Claus and Mallmann[1] gave 146.5° as the fusing point of ortho-nitro-benzoic acid. The free acid had a sweet taste, and dissolved in caustic potash or soda with an intense yellow color. The analysis of the barium salt gave the following results:

I. 0.2366 gram of the salt lost 0.0253 gram H_2O at 160° and gave 0.1050 gram $BaSO_4$.

II. 0.2162 gram of the salt lost 0.0230 gram H_2O at 160° and gave 0.0968 gram $BaSO_4$.

III. 0.1992 gram of the salt lost 0.0210 gram H_2O at 150°. The barium determination was lost.

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 760.

	Calculated.		Found.		
			I.	II.	III.
$(C_7H_7NO_4)_2$	332	63.47	...	...	...
Ba	137	26.20	26.30	26.32	...
$3H_2O$	54	10.33	10.69	10.64	10.54

The salt used in analysis III was recrystallized from water.

A rough estimate was made of the yield from the oxidation. From 8 grams of nitro-toluene oxidized as described above, two grams of unoxidized nitro-toluene were recovered, and barium salts were obtained corresponding to about 1.2 gram of para-nitro-benzoic acid and 1.7 gram of the ortho acid. No great exactness is claimed for these numbers.

Thus the proof was complete that both ortho and para-nitro-toluene are oxidized to the corresponding nitro-benzoic acids by potassium ferricyanide and caustic potash.

It was thought that something might be learned about the relative ease with which the para and ortho compounds are oxidized by oxidizing the portion of nitro-toluene which had been left unacted upon by the mixture. If this should leave only ortho-nitro-benzoic acid, it would indicate that the para compound was most easily acted upon and had been entirely oxidized, leaving only ortho-nitro-toluene. The oxidation was conducted as before and again a mixture of two acids was obtained, one fusing at 139°–140°, and the other at 239°. The amount obtained was not enough for complete purification and analysis, but there can be no doubt that both ortho- and para-nitro-benzoic acids were formed. Hence there is no indication whether ortho- or para-nitro-toluene is oxidized more easily. Both compounds are oxidized in the same manner as by potassium permanganate in alkaline solution.

Oxidation of the Brom-toluenes.

Only an outline of the work done with ortho-brom-toluene will be given here, as, in spite of much time which has been spent on the subject, no decisive result has yet been obtained. The methods in which the attempt has been made to determine whether ortho-brom-toluene is oxidized by the mixture I am studying are as follows: (1) Oxidation of liquid brom-toluene, from Kahlbaum; this contained three per cent. of benzyl bromide (determined by the method described by Jackson[1]), and gave about 1.6 per cent. of the amount of brom-toluene used, in benzoic acid, and a small amount of para-brom-benzoic acid. A careful examination of the barium salts of the acids obtained, based on the solubility of ortho-brom-benzoate of barium in alcohol, failed to show any ortho-brom-benzoic acid. A trace may, however, have been present. (2) Oxidation of brom-toluene nearly freed from benzyl bromide by heating with alcoholic ammonia; this gave chiefly para-brom-benzoic acid and a trace of benzoic acid, but no evidence of ortho-brom-benzoic acid. (3) Oxidation of brom-toluene partly purified from the para compound by boiling for twenty-four hours with an excess of the chromic acid oxidizing mixture; this gave a small amount of an acid fusing above 230°. (4) Oxidation of a brom-toluene boiled for fifty hours with a large excess of the chromic acid mixture; one gram of this brom-toluene, when treated with 25 grams of ferricyanide, gave between 3 and 4 milligrams of an acid for which no satisfactory fusing point could be obtained. By oxidizing a very small portion of the same brom-toluene with potassium permanganate, acids were easily obtained fusing at 246°–248° and at 141°–143°. One gram of *para*-brom-toluene oxidized with 25 grams of the ferricyanide in exactly the same way that was followed with the brom-toluene last mentioned gave 6.4 milligrams of para-brom-benzoic acid.

Different specimens of para-brom-benzoic acid mentioned above fused at 248° to 255°; the purest at 252°–253° (cor.), exactly the same point which was found for a specimen of the pure acid obtained by oxidizing para-brom-toluene with the chromic acid mixture. The benzoic acid fused at 120°, and its character was also established by an analysis of the barium salt.

0.0503 of the salt lost 0.0049 gram H_2O at 130° and gave 0.0305 gram $BaSO_4$.

	Calculated for $(C_6H_5CO_2)_2Ba + 2H_2O$.	Found.
Ba	33.01	33.02
$2H_2O$	8.67	9.02

While these experiments have not yet established whether ortho-brom-toluene is oxidized at all by potassium ferricyanide, and I intend to return to this point as soon as proper material can be obtained, they do show that, if there is any oxidation, it takes place with very great difficulty. The only other possible explanation of the results obtained would seem to be that ortho-brom-benzoic acid is unstable towards this oxidizing agent and is destroyed as fast as it is formed. This explanation was considered very improbable, but it was made the subject of a special experiment. 0.0055 gram of ortho-brom-benzoic acid was boiled for three hours with 25 grams of potassium ferricyanide, 12 grams of caustic potash and 100 cc. of water. The filtrate from the ferric oxide was evaporated somewhat, the potassium ferrocyanide, which crystallized out on cooling, was filtered off, the filtrate acidified with sulphuric acid and extracted with ether. The residue left on distilling off the ether was dissolved in a little ether and the solution evaporated on a watch-glass. It left 0.0048 gram of the acid. This fused, without further purification, at 132°–133°. It was white and dry.

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[1] This Journal, **2**, 4.

It was very noticeable in this experiment that the reduction of the ferricyanide was even more complete than usual, although the boiling was continued no longer than in other experiments, and all oxidation must have been practically confined to action of the ferricyanide on itself. This furnishes a partial explanation of the very small amount of para-brom-toluene which can be oxidized with a given amount of potassium ferricyanide. Evidently the para-brom-toluene is oxidized with greater difficulty than the ferricyanide itself, and hence the oxidizing action is directed chiefly toward the latter until the reduction of the ferricyanide is complete. There is, as it were, a balance struck between the amount of the brom-toluene and the ferricyanide which is oxidized. Of course, the amount of the former cannot be increased by lengthening the time of boiling.

The amount of the para-brom-toluene which can be oxidized by this method is so small that it was difficult to obtain enough of the para-brom-benzoic acid for an analysis. A small amount of the barium salt was prepared from the acid obtained by several oxidations. It was difficultly soluble in water and crystallized in small white leaflets, appearing exactly like the salt prepared from the acid obtained in the usual manner. The analysis was performed with the utmost care on a balance giving constant weights to $\frac{1}{10}$ milligram.

0.0145 of the salt lost no water at 120° and gave 0.0064 gram $BaSO_4$.

	Calculated for $(C_6H_4BrCO_2)_2Ba$.	Found.
Ba	25.5	25.9

All the properties of the acid and salt, so far as studied, agreed exactly with those of the acid and salt prepared in the usual manner. The acid fused at 252°–253° (cor.).

For the purpose of comparison, one gram of toluene (Merck's; boiled 110°–112°) was oxidized with 25 grams of potassium ferricyanide in the same manner as described above. About nine milligrams of benzoic acid were obtained. It fused at 120°.

A summary of the results thus far obtained is as follows:

I. Ortho-nitro and para-nitro-toluene are oxidized to the corresponding nitro-benzoic acids by potassium ferricyanide and caustic potash, as they are by potassium permanganate in alkaline solution and by nitric acid. The oxidation takes place quite readily.

II. Toluene and para-brom-toluene are oxidized by potassium ferricyanide with great difficulty, and the latter with greater difficulty than the former. Ortho-brom-toluene is oxidized, if at all, with very great difficulty.

The effect of the nitro-group upon the toluene molecule deserves a word. It is an effect for which there are some analogies among the other nitro derivatives of benzene, but which, I think, has not been noticed in any case exactly like this before. More than twenty-five times as much of para-nitro-toluene as of toluene itself is oxidized by 25 grams of potassium ferricyanide. This is a good illustration of the fact so often stated, that an atom or group affects all parts of a molecule in which it is situated, no matter how far from it those parts may be.

I cannot conclude without expressing my hearty thanks to Professor Remsen for valuable suggestions given me with reference to this work before it was undertaken, and for the kindness with which he furnished me with some of the materials necessary for these experiments.

UNIVERSITY OF MINNESOTA, *March* 27, 1883.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XIV.—EXPERIMENTS WITH DERIVATIVES OF NAPHTHALENE.

By Ira Remsen.

The facts which have been established by earlier investigations of this series led to the belief that the oxidation of the α- and β-sulphamides of naphthalene with potassium permanganate would yield results of value in connection with some of the interesting questions involved in the isomerism of the substitution products of naphthalene and of phthalic acid. There were three points which it was desired particularly to accomplish in this investigation: (1) to establish, if possible, a direct line of connection between the sulphonic acids of naphthalene and the oxyphthalic acids; (2) to determine the influence of the presence of alkali on the oxidation phenomena; and (3) to determine whether either or both the sulphamine-phthalic acids can yield anhydrides corresponding to the sulphinides described in earlier papers. The part of the investigation, an account of which is here given, has to deal with the best conditions for passing from the sulphamides of naphthalene to the corresponding derivatives of phthalic acid. The more detailed study of these derivatives is now in progress, Mr. E. H. Keiser having undertaken the study of the β-compounds and their transformations, while Mr. H. N. Stokes is engaged in a similar study of the α-derivatives.

Oxidation of α- and β- Naphthalenesulphamides.

By W. J. Comstock.

The lead salts of α- and β-naphthalenesulphonic acids were made and separated according to the directions given by Merz[1] and by Merz and Weith.[2] To make the sulphamides the lead salts were treated directly with phosphorus pentachloride and ammonia. The results were as satisfactory as those obtained by Maikopar,[3] who used the potassium salts. After the action of the ammonia was over, the cooled mixture was poured upon the filter and washed with cold water. The amides were separated from inorganic matter by dissolving in strong alcohol and recrystallising from water. Thus both amides were easily obtained in pure condition with the properties ascribed to them by previous writers.

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[1] Zeitschrift für Chemie, 1868, 393.

[2] Berichte der deutschen chemischen Gesellschaft, **3**, 196.

[3] Zeitschrift für Chemie, 1869, 711.

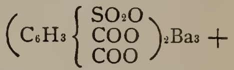
Preliminary experiments with nitric acid as the oxidising agent gave unsatisfactory results, and it was only after we had experienced repeated failures that we finally succeeded with potassium permanganate.

Experiments in the α-series.

Experiment 1.—10 grams of the α-amide were oxidised in neutral solution with 48 grams potassium permanganate in one litre of water. The mixture was kept in the water-bath at 100° until the permanganate was completely reduced. This took place in two hours. After separating the oxides of manganese the solution was evaporated to about 250 cc., acidified with hydrochloric acid and extracted with ether. The extract weighed 3.5 grams, and on recrystallisation from water proved to be pure phthalic acid.

The solution after extraction with ether was evaporated to dryness and extracted with alcohol. The compound extracted was *α-sulphophthalic acid,* as was shown by the formation of the neutral barium salt. The free acid was not obtained pure enough nor in sufficient quantity for examination. It is very soluble in water, and somewhat less soluble in alcohol. It cannot be extracted from aqueous solutions by ether.

Neutral barium α-sulphophthalate,



$\left(C_6H_3\left\{\begin{matrix}SO_2O\\COO\\COO\end{matrix}\right.\right)_2Ba_3 + 8H_2O$. This salt was made by boiling a dilute solution of the acid for some time with an excess of barium carbonate. It is difficultly soluble in boiling water and crystallises on cooling. The crystals appear under a lens to be aggregations of needles, but under the microscope these are seen to be aggregations of small plates, clear and transparent. The air-dried salt lost seven molecules of water below 150°, but retained the other molecule at a much higher temperature.

.277 gram lost at 150° .0342 gram H_2O; at 250° it lost .0039 gram more of H_2O.

	Calculated.	Found.
$8H_2O$	13.83	13.76

.2389 gram anhydrous salt gave .1861 gram $BaSO_4$.

Anhydrous salt.	Calculated.	Found.
Ba	45.82	45.80

The salt is very soluble in dilute hydrochloric acid, and does not yield an acid salt by long standing of the concentrated solution.

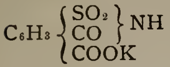
Secondary lead salt, $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}SO_2O\\ COO\end{array}\right\}Pb\\ COOH\end{array}\right. + 1\frac{1}{2}H_2O$. This was prepared by boiling a dilute aqueous solution of the acid with lead carbonate for some time, and filtering while hot from the excess of lead. When the solution cools the salt settles in flocculent form, and afterwards changes slowly into small prismatic crystals. This change takes place more quickly when the flocculent precipitate is collected on the filter and kept in moist condition under a bell-jar for several days. Some of the salt treated in this way and then dried in the air appeared to be entirely changed into the prismatic crystals.

.2644 gram of this air-dried salt lost .0148 gram H_2O at 150° and gave .1701 gram $PbSO_4$.

	Calculated.	Found.
Pb	43.31	43.95
$1\frac{1}{2}H_2O$	5.65	5.60

Experiment 2.—10 grams α-amide were dissolved in 500 cc. of water, with addition of 8 grams potassium hydroxide, and to this were added 48 grams potassium permanganate dissolved in one litre of water. The reduction of the permanganate was complete in about 36 hours at 100°. The solution was treated as in Experiment 1. Some phthalic acid separated out after acidifying, and more was extracted by ether. After evaporating the solution to dryness and extracting with alcohol, a small quantity of the α-sulphophthalic acid was obtained and recognised by means of its neutral barium salt. No sulphaminephthalic acid could be detected.

Experiment 3.—Two portions of nine grams of the α-amide, each dissolved in 450 cc. of water, with 7 grams potassium hydroxide, were treated each with 40 grams potassium permanganate dissolved in 900 cc. of water. The reduction of the permanganate was complete in each case in about twelve hours at 100°. After filtering from the oxides of manganese the portions were united, concentrated to about 350 cc. and acidified with hydrochloric acid. On cooling there separated about five grams of needle crystals about one centimeter long. Upon recrystallisation from water the crystals were much shorter and thicker. These crystals proved to be *mono-potassium α-anhydrosulphaminephthalate*,



$C_6H_3\left\{\begin{matrix}\left.\begin{matrix}SO_2\\CO\end{matrix}\right\}NH\\COOK\end{matrix}\right. + H_2O$. The salt can be easily crystallised from hot water or alcohol. It is insoluble in ether. It was shown to contain both nitrogen and sulphur, and gave off ammonia when fused with potassium hydroxide.

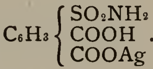
.3126 gram of the air-dried salt lost .0200 gram H_2O at 160° and gave .0950 gram K_2SO_4.

.3969 gram lost .0258 gram H_2O at 160°, and after fusing with KOH and KNO_3 gave .3225 gram $BaSO_4$.

	Calculated.	Found.	
S	11.30	11.16	
K	13.81	13.64	
H_2O	6.36	6.40	6.50

Whether the water which is given off at 160° is water of crystallisation or water of constitution it is impossible to decide. It is certain, however, that after the salt has been heated to 160° an anhydride is left, and it is difficult to see what this can be but a new example of the class of bodies known as sulphinides which have been studied in this laboratory.

Mono-silver α-sulphaminephthalate,



$C_6H_3\left\{\begin{matrix}SO_2NH_2\\COOH\\COOAg\end{matrix}\right.$. This was obtained by adding silver nitrate to the aqueous solution of the above-described potassium salt. The same salt is formed when the silver nitrate solution is acidified with nitric acid. It can be easily crystallised from its hot solutions in water or dilute nitric acid. It crystallises in colorless transparent needles. The air-dried needles did not lose in weight at 180°, and when heated much above that temperature became dark-colored, apparently owing to decomposition.

.2955 gram gave .0903 gram metallic silver.

	Calculated.	Found.
Ag	30.68	30.56

In this case the formation of an anhydride, observed in all similar cases, does not seem to take place.

In the above experiments, the only one in which the sulphamine acid was obtained was that in which the oxidation was made in alkaline solution and without excess of the oxidising agent. In this case also there was found but a small quantity of phthalic acid. It is, of course, possible that the sulphamine acid was formed in the other cases, and the amido group split off by the hydrochloric acid when the solution was evaporated to dryness. At any rate, the proportion of the α-sulphaminephthalic acid formed in the third experiment was much larger than in the others.

Experiments in the β-series.

Experiment 1.—10 grams of the β-amide were dissolved in one litre of water with 7 grams potassium hydroxide, and to this was added one litre of water containing 48 grams potassium permanganate. The permanganate was reduced in about thirty hours at 100°. After separating the oxides of manganese and concentrating to about 250 cc. the solution was acidified with hydrochloric acid. It deposited on cooling about three grams of small prismatic crystals. After recrystallising once from water these crystals contained sulphur, but no nitrogen, and proved to be *di-potassium β-sulphophthalate*, $C_6H_3\left\{\begin{array}{l}SO_2OK\\COOK\\COOH\end{array}\right. + 2H_2O$. The salt is very easily soluble in water and almost insoluble in both cold and hot alcohol.

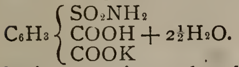
.3207 gram of the air-dried salt lost .0314 gram H_2O at 150° and gave .1572 gram K_2SO_4.

	Calculated.	Found.
K	21.83	22.00
$2H_2O$	10.05	9.79

The salt has a strongly acid reaction, and its aqueous solution dissolved potassium carbonate with effervescence, but no crystallised neutral salt could be obtained from the very strong solution.

A very small quantity of phthalic acid was obtained from the solution by extraction with ether after the separation of the acid potassium sulphophthalate; and although the residue after evaporating the solution still contained some organic matter, this could not be separated by extracting with hot or cold alcohol.

Experiment 2.—24 grams of the β-amide were dissolved in two litres of water with 16 grams potassium hydroxide, and oxidised with 108 grams potassium permanganate dissolved in two litres of water. The oxidation was made in two equal portions, and in each portion the permanganate was reduced in about twelve hours. After treating in exactly the same manner as in the experiment preceding, the crystals obtained were entirely different in appearance, and proved to be *mono-potassium β-sulphaminephthalate,*



$C_6H_3\left\{\begin{matrix}SO_2NH_2\\ COOH\\ COOK\end{matrix}\right. + 2\frac{1}{2}H_2O$. The salt crystallises in silky needles, having sometimes a length of half a centimeter and collected in groups radiating from a centre. It had a light straw color after three recrystallisations. It is easily soluble in water with a strongly acid reaction, and when fused with potassium hydroxide gives off ammonia.

.2800 gram of the air-dried salt lost .0401 gram H_2O at 180° and gave .0754 gram K_2SO_4.

	Calculated.	Found.
K	11.92	12.09
$2\frac{1}{2}H_2O$	13.72	14.32

But a small quantity of phthalic acid was found in this case, so that there must still have been a considerable quantity of the sulphaminephthalate in the solution, which was shown to contain organic matter.

In the β-series as in the α-series the most favorable condition for obtaining the sulphamine acid seems to be maintained when no excess of permanganate is present beyond the quantity required theoretically to convert the amide into the corresponding substituted phthalic acid.

It is impossible to state certainly from this work which of the sulphophthalic acids Loew obtained[1] by heating phthalic acid with sulphuric anhydride. But from the conduct of the lead salt of his acid, which he states was decomposed with separation of lead sulphate by gently warming the aqueous solution, it could not have been the α-acid obtained by me, for the lead salt of this acid was boiled for several hours without decomposition.

The mono-potassium β-sulphaminephthalate is probably the same salt as that obtained by Jacobsen[2] by oxidising sulphamine-orthotoluic acid, although he has not described his salt in sufficient detail to make the identity certain.

[1] Annalen der Chemie, **143**, 257.

[2] Berichte der deutschen chemischen Gesellschaft, **14**, 42.

ON THE PREPARATION AND REACTIONS OF CROTONALDEHYDE.

By Spencer B. Newbury.

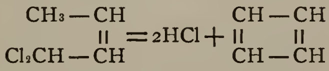
Two years ago I published in the *Comptes rendus* (Paris, Jan. 24th, 1881), the description of a method for the preparation of crotonaldehyde, founded upon Wurtz's discovery that aldol, $CH_3CHOH CH_2CHO$, is completely resolved into water and crotonaldehyde. This method, which subsequent experiments have led me to modify somewhat, is briefly as follows:

One volume of aldehyde (or paraldehyde) is mixed with one volume of water and two volumes of concentrated hydrochloric acid, and the whole allowed to stand for some days at the ordinary temperature of the laboratory. In case aldehyde is employed the solution must be kept cold during the addition of the acid; with paraldehyde no such precaution is necessary. On standing, the mixture assumes a brown color, and becomes finally quite dark and opaque. The progress of the condensation may be tested from time to time by neutralizing a small portion of the solution with sodium carbonate. The right point has been reached when the neutralization causes the separation of a thick oily layer, which becomes indistinctly crystalline after standing some hours. The whole is then neutralized, the layer of higher products of condensation removed by skimming or filtration, and the solution exhausted by shaking repeatedly with ether. On distilling off the ether, aldol, mixed with paraldehyde and some higher products (dialdan, &c.) remains in the retort. By distillation under reduced pressure the aldol may be obtained nearly pure, as a thick, syrupy, colorless liquid. The fraction which passes over between 90° and 110° under a pressure reduced to 2 cm. of mercury is sufficiently pure for the preparation of crotonaldehyde.

The yield of aldol seems to be somewhat greater if less acid be employed, but the reaction proceeds much more slowly. Under favorable circumstances I have obtained 450–500 grams of aldol from 2 kg. of paraldehyde. The yield of crotonaldehyde is about 50 per cent. of the aldol employed, hence from 10 to 12 per cent. of the aldehyde used.

Aldol boils, with more or less complete decomposition into water and crotonaldehyde, at about 185°. This decomposition begins at about 140°, and by keeping the substance at this temperature in an oil-bath, and allowing the products of decomposition to distill over, the maximum yield of crotonaldehyde may be obtained. The product is then freed from water by means of calcium chloride or potassium carbonate, and rectified. Pure, dry crotonaldehyde boils at 105°.

The derivatives of crotonaldehyde have been but little studied, chiefly for the reason that they are for the most part very unstable. Kekulé[1] obtained the compound "crotonylene chloride," or rather dichloropseudobutylene, $CH_3-CH=CH-CHCl_2$, by the action of phosphorus pentachloride on crotonaldehyde. He describes in the above paper his repeated attempts to remove the two atoms of chlorine from the above compound by boiling with alcoholic potash, by which he hoped to obtain diethylene, according to the reaction:



$$\begin{array}{r} CH_3-CH \\ \| \\ Cl_2CH-CH \end{array} = 2HCl + \begin{array}{c} CH-CH \\ \| \qquad \| \\ CH-CH \end{array}$$

In this he was unsuccessful, for after boiling for many hours the substance was not materially affected. In my own experiments I found the dichloro compound to be equally indifferent to the action of an alcoholic solution of sodium ethylate, while my endeavor to derive a chlor-acetal from crotonaldehyde by passing gaseous HCl through an alcoholic solution of the latter was also unsuccessful; the solution became dark brown in color, and the resulting product decomposed completely on heating.

By the action of bromine on the dichloropseudobutylene described by Kekulé, I obtained a heavy, oily liquid, the analysis of which agrees closely with that required by the formula $CH_3CHBrCHBrCHCl_2$, or dichloropseudobutylene dibromide. This compound is at once decomposed on heating above 100°, and hence cannot be distilled. On boiling with a dilute solution of potassium carbonate, carbon dioxide was evolved, but after several days' boiling the resulting product still showed the presence of both Cl and Br. One fraction, boiling at 115°-120°, showed approximately the composition C_4H_6BrClO.

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[1] Liebig's Annalen, **162**, 99.

Crotonaldehyde combines readily with bromine, forming a heavy, oily liquid, the vapor of which attacks the mucous membrane of the nose and eyes most painfully. This compound shows the composition $CH_3CHBrCHBrCHO$. It decomposes at once on heating, and all my attempts to replace the bromine atoms by hydroxyl groups were unsuccessful.

Cornell University, *April*, 1883.

ELECTROLYSIS OF BISMUTH SOLUTIONS.

By N. Wiley Thomas and Edgar F. Smith.

In estimating bismuth in the electrolytic way, solutions of the sulphate, alkaline solutions of the citrate, and the latter in presence of free citric acid were used.

I. A weighed quantity of bismuthous oxide was dissolved in about 1 cc. conc. sulphuric acid and then diluted to 100 cc. with distilled water. 10 cc. of this solution contained .0358 gram metallic bismuth. In two experiments with this solution 10 cc. of the same were placed in a small platinum crucible surrounded by a stout copper wire leading from the zinc pole of a three (one quart) celled bichromate battery. Into the solution dipped a platinum wire connected with the carbon pole. The current ran three hours, was then interrupted and the liquid quickly removed from the vessel. The deposited metallic bismuth, compact and perfectly regular, was washed first with water, then with alcohol, after which it was dried and weighed.

Found, *a*, .0354 gram Bi; *b*, .0358. Required, .0358 gram Bi.

In two additional experiments, instead of placing the bismuth solution in a crucible it was put into a beaker glass, diluted up to 100 cc. with water, and a platinum crucible connected with the zinc pole was suspended in the liquid. The platinum wire from the carbon pole extended down below the crucible. The solution being so much more dilute than in *a* and *b*, the current was allowed to run five hours before being interrupted. The crucible, upon the outside of which the metal had deposited in a homogeneous form, was then removed, the coating washed as before, dried and weighed.

Found, *c*, .0310 gram Bi; *d*, .0355. Required, .0358.

The liquid remaining from *c* gave a brownish coloration with hydrogen sulphide.

This method can be employed with satisfactory results by using moderately concentrated solutions and having the wire from the carbon pole not too far removed from the vessel upon which the metal is to be deposited.

II. Bismuth hydrate was dissolved in conc. citric acid and the liquid then made alkaline with sodium hydrate. The quantity of metal in solution was determined and definite portions of the liquid then electrolysed.

Found, 1, .0356; 2, .0358; 3, .0358. Required, .0356.

The slight difference is probably due to the difficulty experienced in removing the alkali and to errors in weighing. Only two of the previously mentioned cells were used. The time allowed for the precipitation was three hours. The deposit in each case was compact and regular.

III. An alkaline citrate solution of bismuth was acidified with citric acid and definite portions of it subjected to the action of the current. Two cells were employed and the average time for precipitation was two and a half hours. Required Bi = .0356 gram; found:

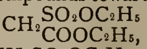
1.—.0358
2.—.0353
3.—.0352
4.—.0358
5.—.0356
6.—.0358
7.—.0357
8.—.0356
9.—.0357
10.—.0358
11.—.0358
12.—.0356

Heat does not hasten the precipitation. In some instances when the current was not very brisk a slight deposition of oxide upon the wire was observed, but this invariably disappeared before the action of the current was interrupted.

Muhlenberg College, Allentown, Pa., *February* 9, 1883.

ON SOME PROPERTIES OF PHENYLSULPHONACETIC ETHERS.

By A. Michael and A. M. Comey.

The important investigations of Geuther, Wislicenus, V. Meyer, and others, on ethyl acetyl acetate and nitroalkanes have shown that in organic compounds the properties of the hydrogen of a hydrocarbon group are dependent on the nature of the groups joined to the same carbon. While in ethyl acetate the acid action of the group $COOC_2H_5$ does not suffice to render a hydrogen of the methyl group sufficiently negative to be replaceable by metals, this property is shown when the combined action of the acetyl and $COOC_2H_5$ groups, or two of the latter, exert their influence on a methylene group. We have considered as worthy of investigation the question, whether in organic compounds the replaceability of hydrogen by metals only occurs under the combined influence of two organic negative radicals; or if these radicals may be wholly or partially replaced by radicals of inorganic acids without loss of this property. The present note will show that the acetyl group of ethyl acetyl acetate when replaced by the acid radical $C_6H_5SO_2$, the sulphonether still has the property of forming metallic derivatives. We hope in the course of our investigation to examine the behavior of the following compounds towards sodium or sodium ethyloxide, $CH_2(SO_2OC_2H_5)_2$,  $CH_2\begin{matrix}SO_2OC_2H_5\\COOC_2H_5\end{matrix}$, $CHCl_2COOC_2H_5$,[1] $CH(OC_2H_5)_2COOC_2H_5$ and $CH_3SO_2OC_2H_5$.

The phenylsulphonacetic ether used in our experiments was prepared by the action of ethyl chloracetate on sodium phenylsulphinate.[2] To an alcoholic solution of the sulphinate, obtained by adding the equivalent amount of ethylsodiumoxide to a solution of the acid in absolute alcohol, the molecular weight of ethyl chloracetate was added and the mixture heated for four or five hours in a hot water-bath. The sodium sulphinate dissolved on heating, and a deposition of sodium chloride was soon noticed. After the reaction was over the alcohol was distilled off and the contents of the flask shaken out with water. The insoluble oil cannot be purified by distillation, as it undergoes decomposition below its boiling point. If it is allowed to stand for several hours, large crystals separate out of the oil, which may be removed; or the oil allowed to stand for several days, when it solidifies almost completely. The yield obtained was about 80 per cent. of the amount indicated by the theory. The substance was purified by crystallisation from absolute alcohol. A sulphur estimation, made by the method of Carius, gave the following result:

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[1] It is not impossible that the difference of the behavior of some organic haloids towards H_2O and caustic alkalis may be due to the action of the halogen on the hydrogen. Thus, to take an example, the first phase of the action of KOH on ethylene bromide may be the formation of a certain amount, dependent on the law of mass and affinity, of the compound $CHKBr-CH_2Br$, which immediately splits into $CHBr-CH_2$ and KBr. A series of reformations and decompositions of $CHKBr-CH_2Br$ would then take place until all is decomposed. That this cannot happen in the action of water on ethylene bromide is evident. I am well aware that this view is open to serious objections, but believe it to be worthy of consideration.—A. M.

[2] That sulphones are obtained in this manner was first shown by P. Claesson (J. pr. Chem. [2], **15**, 223). R. Otto (Ber. 1880, 1272), and later, S. Gabriel (*ibid.* 1881, 883), have apparently overlooked that research.

0.2292 gram of substance dried *in vacuo* gave 0.2360 gram of $BaSO_4$.

	Theory for $C_6H_5SO_2CH_2COOC_2H_5$.	Found.
S	14.04	14.14

Ethyl phenylsulphonacetate crystallises from alcohol in clusters of long prisms. It is insoluble in hot water, soluble in hot, but slightly in cold alcohol. The substance melts at 45°. Boiled with alkalis, the corresponding salt is formed, which, treated with acids, yielded phenylsulphonacetic acid.

The behavior of the ether towards sodium was first examined, but without obtaining very satisfactory results. On a solution of the ether in benzene no action was noticed in the cold; when the solution was heating to boiling, the sodium acted but very slowly, forming a white amorphous substance. Better results are obtained by mixing solutions of the ether and ethylsodiumoxide, in proportions of equal molecules in absolute alcohol; a method, as Conrad and Limpach[1] have shown, which gives the sodium derivative of ethyl acetyl acetate. A mixture of equivalent amounts of the two substances dissolved in absolute alcohol soon solidifies to a mass of voluminous white needles. They were filtered, washed well with absolute alcohol and dried *in vacuo*. A sodium estimation gave the following result:

0.6935 gram of substance gave 0.1955 gram of Na_2SO_4.

	Theory for $C_6H_5SO_2CHNaCOOC_2H_5$.	Found.
Na	9.30	9.13

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[1] Annalen der Chemie, **192**, 153.

Ethyl sodiumphenylsulphonacetate is sparingly soluble in cold, moderately in hot alcohol. In water it is very soluble; the aqueous solution acidified gives a precipitate of the original ether, melting at 45°. An alcoholic solution of the compound when boiled gradually solidifies to a gelatinous mass, which is also obtained when hot solutions of the alcoholate and ether are mixed. This sodium product when heated gives a sublimate melting at 85°; when treated with acids, a product which is not the original ether. It will be further examined.

In the present note we shall confine ourselves to the proof that the sodium in the above compound can be replaced by monad hydrocarbon radicals, and reserve for a second paper to show that in the proper uses of the above class of compounds valuable methods for the syntheses of organic compounds have been found.

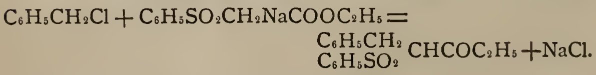
To an alcoholic solution of ten grams ethyl phenylsulphonacetate a solution of one gram sodium in absolute alcohol and five grams benzyl chloride were added. The precipitate of the sodium derivative dissolved on heating in a water-bath, and in a short time the formation of sodium chloride began. After heating for several hours the condenser was inverted and the alcohol evaporated. The oil remaining in the flask was poured in water; it gradually hardened to a crystalline mass. The substance was purified by crystallisation from absolute alcohol. On analysis it gave the following numbers:

I. 0.2300 gram of substance, dried *in vacuo*, gave 0.5362 gram CO_2 and 0.1228 gram of H_2O.

II. 0.2138 gram gave (Carius's method) 0.1442 gram $BaSO_4$.

	Theory for $C_{17}H_{18}O_4S$.	Found.
C	64.14	63.59
H	5.66	5.93
S	10.06	9.26

The formation of the substance may be represented as follows:



$$C_6H_5CH_2Cl + C_6H_5SO_2CH_2NaCOOC_2H_5 = \begin{matrix} C_6H_5CH_2 \\ C_6H_5SO_2 \end{matrix} CHCOC_2H_5 + NaCl.$$

Ethyl benzylphenylsulphonacetate is insoluble in cold and hot water; sparingly in cold, readily in hot alcohol. From alcohol it is obtained as short white prisms, melting at 95–96°. Treated with an alcoholic solution of sodiumethyloxide it yields a sodium derivative, which is more soluble than the corresponding phenylsulphonether derivative. When heated with benzyl chloride the sodium compounds give the dibenzyl derivative, melting at 118°.

The mono-benzylether saponifies with difficulty. Heated with aqueous sodium hydrate, the decomposition of several grams was incomplete, even after boiling for eight hours. The saponification is easily effected by heating the substance with an excess of alcoholic caustic soda for several hours in a closed tube at 100°. The crystalline salt, which gradually separated from the solution on heating, was dissolved in water and the acid liberated by addition of a mineral acid. The examination of the substance showed that it contained no sulphur, and that it possesses all the properties of cinnamic acid. An analysis proved the identity beyond a doubt.

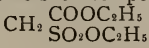
0.1982 gram of substance gave 0.5282 gram of CO_2 and 0.1010 gram of H_2O.

	Theory for $C_6H_5CHCHCOOH$.	Found.
C	72.97	72.69
H	5.40	5.64

The formation of cinnamic acid may be represented as follows:

$$C_6H_5CH_2CH(SO_2C_6H_5)COOC_2H_5 + 2KOH$$
$$= C_6H_5CHCHCOOH + C_6H_5SO_2K + C_2H_5OH + H_2O.$$

This decomposition seems to be characteristic for this class of compounds. According to Valet[1] phenylsulphopropionic acid, $C_6H_5C_2H_3SO_2OHCOOH$, heated with caustic potash, decomposes easily in the potassium salts of cinnamic and sulphurous acids, a reaction which is perfectly analogous to the above described.

The proof that one of the hydrogens of the methylene group of ethyl phenylsulphonacetate may be replaced by sodium, renders it extremely probable that such compounds as $CH_2(SO_2OC_2H_5)_2$, $CH_2(SO_2C_6H_5)_2$ and  $CH_2\begin{smallmatrix}COOC_2H_5\\SO_2OC_2H_5\end{smallmatrix}$ are likewise endowed with this property.

TUFTS COLLEGE, MASS., *April* 29, 1883.

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[1] Annalen, **154**, 70.

REVIEWS AND REPORTS.

Analytical Chemistry.

Sulphur.—In order to determine the total amount of sulphur in illuminating gas, Theodore Poleck[1] recommends aspirating the products of combustion from an ordinary Bunsen burner, through an inverted funnel leading to a dilute solution of caustic soda to which bromine has been added. The sulphur dioxide is oxidized to sulphuric acid by this means, and may be determined as barium sulphate. The apparatus is inexpensive as compared with the usual forms used for this purpose, and it has been used by the author with satisfactory results since 1875.

A new method for determining Sulphur in Organic Bodies.—In the endeavor to furnish a method for determining sulphur in organic substances which shall be free from the objections to the methods of Liebig, Fahlberg and Iles, Weidel and Schmidt, and others, Peter Claësson[2] proposes the complete oxidation of the substance in a current of oxygen and nitric oxide, *i. e.* nitrogen tetroxide gas. A combustion tube somewhat longer than the furnace, is drawn out at one end and bent at a right angle. Next to the bend a roll of platinum gauze 7 centimetres long is placed; 10 centimetres from this is a boat containing fuming nitric acid; about 10 centimetres farther another roll of platinum gauze. After this is a third roll, and close beyond it the boat containing the sulphur compound. Last is a fourth roll of gauze. The bent end of the tube dips into water in a small flask, and the other end is closed with a stopper admitting the connecting tubes to the oxygen and nitric oxide supplies. After filling the tube with the mixed gases, the platinum roll on either side of the nitric acid boat is heated to low redness, then the boat farthest from the substance. This order of heating is particularly necessary when oxidizing substances that are easily volatile, as the primary oxidation products are very apt to strike back. The tube is then heated in the usual order of a combustion. The color of the tube between the two boats serves as an indicator: if the red color disappears the combustion must go more slowly. The nitric acid in the boat acts as a reserve; the hot gases in passing over it always take up enough oxygen compounds to complete the oxidation of any unburned particles. If the combustion goes slowly there is no appearance of flame, but it may be hastened considerably without danger. With aromatic substances, particularly naphthalene compounds, it may happen that the substance be converted into a nitro compound and this then burnt like tinder; but even in such a case the oxidation is complete if there is sufficient nitric acid in the boat. At the end of the combustion the heating is extended forward until all the nitric acid, and the sulphuric acid formed in the reaction, have distilled over into the flask. After cooling, the contents of the flask and the washings of the tube are evaporated to dryness, and after dilution with water the sulphuric acid is determined as barium sulphate.

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[1] Zeitschrift für analytische Chemie, **22**, 271.

[2] *Ibid.* 177.

Nitric Acid.—C. Böhmer[1] describes a new method of estimating nitric oxide gas obtained by the reduction of nitric acid. Of the many methods that have been proposed for the estimation of nitric acid, those which are capable of the most extensive application, and which also yield the best results, depend on the reduction of nitric acid by ferrous chloride. Several processes have been used for carrying out this reaction. Pelouze treated the nitric acid with an excess of ferrous chloride and determined how much remained unaltered. C. D. Braun determined the amount of ferric chloride formed at the expense of the nitric acid, and finally Schlösing determined the quantity of nitric oxide formed by reconverting it into nitric acid, and F. Schulze recommended measuring the volume of nitric oxide itself. In an earlier paper[2] Böhmer has shown that chromic acid is an excellent absorbent for nitric oxide, and on this fact he now bases a method for determining the amount of gas yielded by nitric acid. The nitrate or nitric acid is decomposed in the usual way, and the resulting gas, after being dried by calcium chloride, is absorbed in a Liebig's potash bulb containing a concentrated solution of chromic acid, and the nitric oxide determined by the increase in weight.

Phosphoric Acid.—A new method for determining phosphoric acid in superphosphates, volumetrically, has been proposed by A. Mollenda.[3] The method consists in finding the amount of a standard solution of sodium carbonate necessary to neutralize the acid phosphate of calcium which forms the soluble portion of the superphosphate. In order to prevent the precipitation of calcium carbonate from any sulphate of calcium that may be present, the entire amount of calcium is precipitated by sodium oxalate and the acidity of the resulting mono-sodium phosphate determined. If there is free sulphuric or phosphoric acid in the superphosphate, sodium carbonate is added before titration until the liquid becomes slightly turbid.

Calcium and Strontium.—D. Sidersky[4] bases a method for the separation of calcium from strontium on the statement that on adding a mixture of sulphate and oxalate of ammonium to a solution of strontium, the latter is all precipitated as sulphate; on the other hand, if added to a solution of a calcium salt, only oxalate is precipitated. If the mixture is added to a solution containing both strontium and calcium, the former is precipitated as sulphate and the latter as oxalate. The two precipitates are separated by the solubility of the oxalate in acids.

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[1] Zeitschrift für analytische Chemie, **22**, 20. [2] *Ibid.* **21**, 212. [3] *Ibid.* **22**, 155. [4] *Ibid.* 10.

Preservation of Ferrous Sulphate.—A. Gawalovski[1] recommends placing a glass tube half filled with glass wool and an alkaline solution of pyrogallic acid in the crystals so that the mouth reaches somewhat above them. If the jar is then closed tightly the ferrous sulphate will remain unaltered for two or three years.

Copper and Zinc.—It has been shown by G. Larsen[2] that copper and zinc can be separated by one precipitation with hydrogen sulphide if hydrochloric acid is added to the solution of hydrogen sulphide with which the precipitate is washed. Emil Berglund[3] has studied this method independently, and finds that it holds good when a smaller amount ($\frac{1}{10}$ vol.) of hydrochloric acid is added to the wash water than recommended by Larsen, and further that zinc is not precipitated with copper if the amount of hydrogen sulphide in the wash water is small.

Titanium.—A method has been proposed by A. Weller[4] for the detection and estimation of titanium which is based on its reaction with hydrogen peroxide. When precipitated titanic acid is treated with a neutral solution of hydrogen peroxide, it changes to a lemon-yellow color; a concentrated acid solution of titanium gives a deep reddish-yellow color with hydrogen peroxide, without the evolution of any gas. This reaction is due to the formation of a higher oxidation product than titanic acid, and was announced by Schönn,[5] who recommended it as a characteristic test for hydrogen peroxide, but according to Weller the converse use furnishes a test for titanium compounds which is the most delicate known.

A few drops of hydrogen peroxide cause an orange-red coloration in a sulphuric acid solution of one milligram of titanic acid. With $\frac{1}{10}$ milligram the color is a distinct yellow, and even $\frac{1}{50}$ of a milligram can be detected. Tantalic and niobic acids and zirconium oxide, which often accompany titanic acid in minerals, give no similar reaction. The only substances which yield a similar color are vanadic and molybdic acids, and although in these cases the reactions are not so delicate, their absence must be insured in testing for titanic acid. In testing for very minute quantities of titanium, iron salts and other colored substances must of course be removed.

In order to use the reaction for estimating quantities of titanic acid, the depth of color is compared with solutions containing known amounts of titanic acid according to ordinary colorimetric methods. The great advantage of the method lies in the fact that it admits of the detection and estimation of titanic acid without the difficult separation from niobium and tantalum, and from zirconium, for which no exact method is known.

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[1] Zeitschrift für analytische Chemie, **22**, 33.

[2] *Ibid.* **17**, 312.

[3] *Ibid.* **22**, 185.

[4] Berichte der deutschen chemischen Gesellschaft, **15**, 2592.

[5] Zeitschrift für analytische Chemie, **9**, 41.

Vanadium.—A new method for the separation of vanadic acid from metals has been proposed by W. Halberstadt.[1] Like Classen's method for the separation of arsenic and phosphoric acids from the metals, it is based on the fact that when a mixture of the acid and metals is heated with ammonium oxalate and acetic acid, the metals are precipitated as oxalates while the acid sought for remains in solution.

The hydrochloric acid solution of vanadic acid is evaporated to dryness, the residue heated with a saturated solution of ammonium oxalate in water, and a few drops of strong acetic acid added till all has dissolved. The liquid is poured into a beaker and heated over a free flame, while acetic acid is added drop by drop until the precipitate ceases to form. If the acetic acid is added too rapidly the precipitate is difficult to wash. After filtering off the precipitate and washing with a mixture of equal parts of strong acetic acid, alcohol and water, the filtrate is evaporated to dryness in a weighed platinum dish, and the residue heated slowly to expel volatile ammonium salts, and then the remaining vanadium oxide is converted into vanadic acid by heating in a current of oxygen.

The method gives good results in presence of barium, calcium, zinc or lead, but not with cobalt, nickel, manganese, magnesium, bismuth, copper or cadmium.

Tungsten.—Otto F. von der Pfordten[2] has published a new method for the estimation of tungstic acid by reduction with zinc and hydrochloric acid to tungsten dioxide. The reduction takes place with more difficulty than the reduction of molybdic acid, and is best effected by using a 27 per cent. solution of hydrochloric acid. The solution first becomes blue, then a black-green, and finally a dark brownish-red, the end product being tungsten dioxide. This is determined by titration with potassium permanganate. If this is done in the usual way, results are obtained which correspond very nearly to a reduction to tungsten dioxide, but are never as high, because the solution is partially oxidized on exposure to air. But the results are quite exact if the titration is conducted according to Zimmermann's process: using an excess of permanganate, for which minute details are given in the original treatise. The method has one disadvantage, inasmuch as only very small quantities of tungstic acid can be used in the reduction, so that the percentage error may easily become large.

Illuminating Gas.—C. von Than[3] has invented a convenient instrument for estimating the amount of illuminating gas that may be present in the air in any confined space. The instrument is, in principle, a porous cylinder so arranged that the diffusion into it of any gas with a density different from air gives an indication on an open manometer.

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[1] Zeitschrift für analytische Chemie, **22**, 1.

[2] Berichte der deutschen chemischen Gesellschaft, **16**, 508.

[3] *Ibid.* **15**, 2790.

The Detection of Acetal.—M. Grodski[1] bases a method for detecting acetal on the fact that acetal itself gives no iodoform reaction; but when treated with an acid, both its decomposition products, alcohol and aldehyde, do yield iodoform when further treated with iodine in alkaline solution. By acidifying an aqueous solution of acetal with a few drops of hydrochloric acid, and adding caustic soda and a solution of iodine, the iodoform can be recognized even when 1 cubic centimetre of $\frac{1}{10}$ per cent. acetal solution is used.

RECENT INVESTIGATIONS ON URANIUM.

Conclusive evidence as to the correct atomic weight of uranium has, until within the last year, been wanting.

As a result of the analytical investigations of Peligot, Wertheim and Ebelmen, the number 120 was for some time believed to be correct. Later, Mendelejeff called the attention of chemists to the fact that by assuming the correctness of the atomic weight 120, no suitable place could be assigned to uranium in his periodic scheme of the elements. This fact, together with a consideration of some of the properties of uranium, *e. g.* its high specific gravity, the difficult reduction of its oxides, the existence of a volatile chloride, etc., induced Mendelejeff to double the number heretofore accepted, thus placing uranium in the group including oxygen (typical), chromium, molybdenum and tungsten. To prove or disprove the correctness of his views Mendelejeff invited and recommended further investigation of uranium and its compounds.

Clemens Zimmermann[2] has responded to this invitation; and, in the first place by pointing out numerous analogies between compounds of uranium and those of chromium and other members of the same group, in the second place by directly determining the atomic weight to be 240, has justified the opinions of Mendelejeff.

The two fundamental oxides of uranium, namely the dioxide UrO_2, and the trioxide UrO_3, differ markedly, in that the former is strongly basic in character, while the latter possesses acid properties corresponding to the dioxide in the series of uranous salts, while the acid-forming oxide UrO_3 gives rise to the uranates.

In considering what place should be allotted to uranium in Mendelejeff's system, the following observation is of primary importance; *i. e.* while chromium, molybdenum and tungsten form well crystallised chromates, molybdates and tungstates, and not only normal (M_2XO_4; $X = Cr$ etc.) but also poly-salts, heretofore only amorphous polyuranates have been prepared. Some of the experiments of Zimmermann had for their object to decide whether normal uranates could be prepared, and whether the normal or the diuranates were crystallisable.

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[1] Berichte der deutschen chemischen Gesellschaft, **16**, 512.

[2] Annalen der Chemie, **213**, 285, and **216**, 1.

Experiments were made on the alkaline uranates, the sodium, potassium and lithium salts being prepared and studied, great care being taken to secure the absolute purity of the substances considered. His results are as follows: Crystallised uranates were obtained; the potassium and sodium salts corresponded to the formula $M_2Ur_2O_7$, while the lithium salt answered to the formula Li_2UrO_4. These uranates have a beautiful orange-yellow color resembling that of powdered potassium dichromate; they are insoluble in water, easily soluble in dilute acids; when strongly heated they become like potassium dichromate, dark red, but on cooling resume their original color. Crystallographically considered they belong, according to Dr. C. Haushofer, to the rhombic or the clinorhombic system.

The normal lithium uranate differs from the potassium and sodium diuranates in the fact that when heated with water it decomposes into the hydroxides of lithium and uranium (uranyl hydroxide). Neither hot nor cold water has any decomposing effect upon the potassium and sodium diuranates.

These experiments show that the mono- and diuranates are analogous in composition and in a number of important properties to the corresponding compounds of chromium, molybdenum and tungsten, and thus one argument is produced in favor of placing uranium in the chromium group. Final evidence on this point can, however, be furnished only by direct determination of the atomic weight.

Zimmermann has observed the vapor densities of the chloride and bromide; in the case of the bromide the following data will serve to indicate the purity of the substance used:

Analysis of bromide:

	In 100 parts.			
	Found.		Calculated for $UrBr_4$.	
Substance used.	Br.	Ur.	Br.	Ur.
1. 0.2685	57.13	42.92	57.14	42.86
2. 0.3187	57.28	42.75	...	...
3. 2.3223	57.17	42.78	...	...

The vapor density was determined according to V. Meyer's method; the figures given below are the results of six determinations:

Vapor densities found, calculated on air as standard: (1), 19.50; (2), 19 33; (3), 19.34; (4), 19.58; (5), 19.44; (6), 19.58.

The mean of these figures is 19.46, which agrees well with the density 19.36 calculated for the formula $UrBr_4$ in which $Ur = 240$.

Equally satisfactory results were obtained in the case of the chloride, as follows:

Vapor densities found: (1), 13.24; (2), 13.36; (3), 13.40; (4), 13.31, giving the mean 13.3, which differs little from the value 13.21 calculated for the formula $UrCl_4$ ($Ur = 240$).

If, however, these halogen compounds contained in the molecule two atoms of uranium instead of one, the atomic weight of the element would be 120, and therefore additional evidence must decide whether 120 or 240 is to be preferred. This necessary evidence is furnished by the following determination of the specific heat of metallic uranium, Bunsen's ice calorimeter being employed. The mean of three determinations gave the figure 0.02765 for the specific heat. Multiplying this figure by 240, the atomic heat 6.64 is obtained, and this does not differ widely from the mean atomic heat, 6.4, of elements which conform to the law of Dulong and Petit.

The atomic weight 240 seems then to be firmly established, and the insertion of uranium into the chromium group no longer requires the aid of hypothesis.

In the course of these investigations Zimmermann has studied carefully the chemical conduct of the uranous salts, and finds that incorrect statements in regard to many reactions are to be found in the text-books. The uranous chloride and bromide in perfectly pure condition were used. The following statements give the results: the matter in parenthesis gives the reactions as heretofore accepted.

Potassium or sodium hydroxide produces in solutions of uranous salts a voluminous clear green (dark brown to blackish-brown) precipitate of uranous hydroxide, insoluble in excess of the reagent. This precipitate changes rapidly in contact with the air into brownish-black uranoso-uranic hydrate, which after some time becomes yellow potassium or sodium uranate.

Ammonia produces likewise a clear green, flocculent (dark brown) precipitate which undergoes the same changes as those produced by the fixed alkalies.

Secondary potassium or sodium carbonate causes the formation of a whitish-green precipitate, which by heating becomes dark in consequence of oxidation. Primary alkaline carbonates produce a similarly colored precipitate which easily dissolves in excess of the reagent, but by heating is again precipitated with partial oxidation.

Ammonium carbonate produces a whitish-green precipitate, easily soluble in excess and not precipitated again by warming.

Ferrocyanide of potassium creates immediately a yellowish-green (reddish-brown) precipitate, which gradually becomes reddish-brown in consequence of oxidation.

Ferricyanide of potassium effects immediately the formation of a reddish-brown precipitate (not immediately, but only after some time).

The addition of tartaric acid to solutions of uranous salts prevents the formation of a precipitate by ammonia, ammonium sulphide and fixed alkalies, the solution not becoming dark-colored (the solution is by such means colored dark or brown).

Ammonium sulphide causes a clear green precipitate, which rapidly becomes dark brown, and by heating black.

Barium carbonate precipitates uranous salts perfectly in the cold. This series of investigations on uranium has been very fruitful in valuable results, among which may be mentioned, in addition to those already given, an important modification of the Margueritte method of determining iron, and also new methods of determining molybdic, tungstic and phosphoric acids, which methods have been fully worked out by certain other chemists associated with Zimmermann. W. C. D.

THE SYNTHESIS OF MINERALS AND ROCKS.[1]

The ideal development of almost any department of scientific inquiry may be divided into three distinct stages. The first period of simple observation is succeeded by one of analysis, while both are rounded out and completed by the final period of synthesis. In the case of the majority of the natural sciences it has thus far been possible to attain to only the first or second of these stages, but chemistry may boast that she has already made great progress into the third. What astounding results synthesis has yielded in the study of organic compounds is universally recognized, and to judge from the progress already made the inorganic field seems scarcely less promising.

Since the year 1801, when Sir James Hall succeeded in transforming common limestone into marble, there has been a continued effort to obtain by artificial means the minerals occurring in nature. These efforts have been attended by the most marked success, especially in France, where during this century wellnigh all the known mineral species have been successfully reproduced, the same result having often been attained by methods of the most diverse character. In the book before us the authors present a concise resumé of all that has thus far been accomplished by others in this direction, as well as many very interesting results of their own experiments in mineral synthesis, together with a complete bibliography of the whole subject. They have, however, not stopped here. Not being content with the reproduction of minerals as individual species, they have sought to combine them in their natural associations, thus imitating in the laboratory the processes of nature in the formation of the earth's crust. Here they were again successful, and by their experiments have thrown so much light upon questions of no less import to the chemist than to the mineralogist and geologist that it is to their detailed description (pp. 1–80) that the principal interest of the present work attaches.

The first chapter—*a General Introduction*—opens with a statement of five conditions which an artificial mineral product must fulfil in order to be a successful synthesis. 1st. It must be identical in its chemical composition with the natural mineral imitated. 2d. The two must also be crystallographically identical. 3d. Their internal structure, *i. e.* cleavage, inclusions, etc., must be the same. 4th. The artificial minerals must follow the same laws of association as the natural ones. 5th. The conditions of the artificial operation must be compatible with the circumstances under which the natural products were formed.

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[1] Synthèse des Minéraux et des Roches, par F. Fouqué et A. Michel-Lévy. Paris, 1882.

These conditions are followed by a classification of syntheses into intentional and accidental, which in turn is succeeded by an enumeration of several causes to which, during late years, the rapid advancements made in rock synthesis have been largely due. These are: 1st. The introduction of the microscopical examination of rocks, whereby the relative age of the mineral constituents has been revealed, and thus many valuable hints obtained as to the mode of operation, as well as a means of accurately studying the products. 2d. The recent improvements in laboratory appliances. 3d. The gradual overthrow of the traditional idea that the methods of nature are altogether inscrutable, and that any imitation of results accomplished by the joint agency of indefinite time and enormous pressure is out of the question in the laboratory.

Various ways in which synthesis has been of special utility in the study of natural products, by the interpretation of obscure facts, etc., are then noted, while the chapter closes with a classification of all the methods thus far employed in the artificial reproduction of inorganic bodies, as follows:

I. Those producing a molecular change in *solid* bodies.

(*A*) Without chemical action, *e. g.* monoclinic sulphur changing to rhombic.

(*B*) With chemical action, *e. g.* marble produced from limestone.

II. Those producing a molecular change in *fused* bodies.

(*A*) Without chemical action.

(1) Without a solvent, *e. g.* fused silicates, as felspar.

(2) With a solvent, *e. g.* carbon changed to graphite in melted iron.

(*B*) With chemical action, orthoclase, etc., from alkaline tungstates and vanadates.

III. Those producing a molecular change in *volatilised* bodies.

(*A*) Without chemical action, *e. g.* sublimation.

(*B*) With chemical action.

(1) The mutual chemical reaction of vapors, *e. g.* steam and iron chloride forming iron oxide.

(2) The action of vapors on a solid body, *e. g.* zircon and corundum, formed by a gas acting as a "*minéralisateur*."

IV. Those producing a molecular change in bodies *dissolved* in water.

(*A*) At ordinary pressure.

(1) By evaporation, *e. g.* salt and gypsum.

(2) By a supersaturated solution.

(3) By variations of temperature.

(4) By chemical reactions.

(*B*) Under high pressure, *e. g.* quartz.

V. Molecular changes produced by a combination of any of the above processes.

The crystalline constituents of the earth's crust are then arranged for purposes in hand in four categories:

1st. The minerals of volcanic rocks, *i. e.* basic (plagioclase) rocks.

2d. The minerals of acidic rocks, *i. e.* quartz and orthoclase rocks.

3d. The minerals of the crystalline schists, *e. g.* gneiss and mica-schist.

4th. Mineral veins.

Now the following statement sums up in a word all we thus far know of mineral and rock synthesis: *The minerals and their associations of the first of these four categories have nearly all been artificially reproduced by simple fusion; those of the last by solution or volatilisation. Those of the two remaining categories have, on the contrary, not yet been artificially obtained.*

The second chapter on the *Artificial Reproduction of the Eruptive Rocks* contains a detailed account of the methods employed and the results obtained by the authors themselves, preceded by a brief notice of experiments previously made by others in this direction.

Daubrée, Vogelsang, Friedel and Saracin all attempted to reproduce quartz and orthoclase by means of superheated alkaline solutions without decided success. Hautefeuille obtained these minerals crystallised out of fused tungstates, vanadates and phosphates of the alkalies; but this method, interesting in itself, throws little light on their geological genesis. Experiments with simple fusion were performed by Sir James Hall (1801), Gregory Watt (1804), Daubrée (1866), and Sorly as late as 1880, leading, however, only to the conclusion that this was *not* the method of nature in the formation of her lavas. The field was therefore practically new when Fouqué and Lévy entered it in 1878.

The apparatus employed by these investigators was comparatively simple, consisting of a furnace of moderate dimensions by Leclerc and Forquignon, heated by a blowpipe supplied by ordinary illuminating gas and driven by a Damoiseau blast. This arrangement was found to fulfil very satisfactorily the two necessary conditions by readily furnishing a high temperature and allowing the same to be maintained for a considerable time. The substances to be fused (either the fundamental chemical constituents of the desired product or pounded minerals) were placed in a very finely divided and well-mixed state in platinum crucibles, which were encased in coverings of fire clay. By properly regulating the furnace any degree of temperature could be obtained at will. Four grades most frequently employed are designated as temperatures Nos. 1, 2, 3, 4, as follows:

No. 1. The temperature of fused platinum; also sufficient to reduce anorthite, leucite and olivine to a vitreous mass.

No. 2. The melting point of steel, where all the felspars except anorthite are fusible.

No. 3. A temperature between the melting points of steel and copper. Pyroxene and nepheline fuse readily.

No. 4. The melting point of copper.

All rock-making minerals when fused and rapidly cooled give a perfectly homogeneous isotropic glass, Some, however, crystallise much more readily than others ; for instance, it was necessary to cool the molten mass very rapidly to prevent pyroxene, enstatite, melilite and nepheline from crystallising, while the felspars required a much longer time to complete their regular molecular arrangement.

After a certain amount of experience had been obtained with the reproduction of individual minerals, their associations were secured by the employment of a principle, already well known to Hall, that *the melting point of a crystallised silicate is in general higher than that of the same chemical compound in an amorphous state.* If, therefore, the molten mass be held for a time at a temperature between the melting point of the least fusible mineral and its glass, this mineral will crystallise out, and then, if the temperature be lowered to just the right point, the next more easily fusible mineral may be obtained in the same way, and so on to the most easily fusible. It is then a general *rule* that the minerals must crystallise out of a molten magma in the inverse order of their fusibilities. This is mostly the case, but occasional apparent *exceptions* deserve to be noticed and explained.

1st. Certain minerals whose point of fusion is very high, as for example leucite, often contain inclusion of much more easily fusible minerals. The explanation here is that these were included as portions of the amorphous magma, which afterwards by a lower temperature assumed a crystalline structure.

2d. Magnetite, and often picotite, appear as inclusions in silicates of two different periods of crystallisation. The explanation of this fact seems to be that certain bases mutually react and change places, so that the fusibility of these minerals is *not* a function of their time of crystallisation.

3d. The most important exception is that certain *silicates* appear in two successive periods or generations, *e. g.* pyroxene and labradorite often appear both as porphyritic crystals and as microliths in the ground mass. The distance between the points of fusibility of a mineral and its glass may be so great as to allow of its crystallising in two periods, *e. g.* a period of very slow cooling before the eruption of a volcanic rock and the period of rapid cooling immediately succeeding its eruption.

In practical experiments it was found that at temperature No. 2, crystals of leucite, anorthite, olivine, magnetite and picotite were obtained ; at temperature No. 3, crystals of labradorite, oligoclase, pyroxene, enstatite, hypersthene, and also magnetite and picotite; at No. 4, crystals of the same minerals, but especially pyroxene, nepheline, melilite and melanite.

The methods for examining these artificial products are in all respects identical with those employed in the science of petrography for the examination of natural rocks.

By judicious combinations of the methods already recounted the authors have thus far succeeded in obtaining eleven distinct mineral associations or rocks, almost exactly reproducing, even in the minutest details of structure, as many widespread natural types.

I. *Andesites.* Mixture: 1 part augite to 4 parts oligoclase, or its equivalent in chemical substances. This was held for three days at temperature No. 3. *Result:* microliths of oligoclase .25 mm. × .015 mm., of augite .06 mm. × .02 mm. arranged without order and a little magnetite in octahedrons.

II. *Labrador Andesites* ("Labradorites"). Mixture: 1 part augite to 3 parts labrador. Temperature and time as in I. The microliths of labrador and augite are larger and stouter. Twins of the former according to the albite law very common. Magnetite much more abundant than in I.

III. *Anorthite Augite Andesite.* Rare in nature, but obtained artificially without difficulty.

IV. *Basalt and Labrador melaphyre.* Two successive stages of fusion at different temperatures were necessary for the production of this rock. A mixture equivalent to 6 parts olivine, 2 augite and 6 labrador was kept for 48 hours at temperature No. 2, *i. e.* above the fusing point of labrador and augite. The product was numerous crystals of olivine, of the usual natural appearance, averaging .5 × .2 mm., imbedded in an isotropic amorphous glass. This was again subjected to temperature No. 4 for 48 hours, when the glassy base was completely transformed into microliths of labradorite and augite. Magnetite and picotite were formed during both stages of fusion.

V. *Nephelinite.* Mixture: 3 parts nepheline to 1.3 of augite. Temperature No. 4, 48 hours; association hexagonal prisms (.02 mm.) of nepheline with microliths (.01 × .004 mm.) of augite. A mixture of 10 parts nepheline and 1 of augite produced, when treated in the same manner, crystals of nepheline, spinel and black garnet (melanite).

VI. *Leucitite.* Mixture: 9 parts leucite and 1 of augite. Temperature No. 2; 3 days. It was not necessary to fuse twice, notwithstanding the ease with which augite melts, because this mineral crystallises so readily and rapidly.

VII. *Leucite tephrite.* A mixture of silica, alumina, potash, soda, magnesia, chalk and iron oxide, equivalent to 8 parts leucite, 4 of labrador and 1 of augite, was fused into a homogeneous glassy mass. This was subjected in successive stages to temperature No. 2 (48 hours); and temperature No. 4 for the same time. During the first stage of the process the leucite, magnetite and picotite crystallised out of the magma. What remained was converted during the second stage into a crystalline groundmass of labrador and augite microliths.

VIII. *Lherzolite.* This rock was produced first by Daubrée in 1866. By a more prolonged cooling the enstatite forms short prisms instead of long needles. However, the rock does not exhibit precisely the same structure as that found in nature. Thus the picotite is in small octahedrons instead of irregular masses, and glass inclusions are much more numerous.

IX. *Meteorites without Felspar.* Two types were reproduced:

1. Kragujewatz type. Olivine, enstatite, magnetite, native iron.

2. Rittersgrün type. Olivine, magnesian pyroxene, enstatite, native iron.

(1) 12 gr. SiO_2; 3 gr. MgO; 5.55 gr. Fe_2O_3; temperature No. 3 for 3 days.

(2) 6 gr. SiO_2; 3 gr. MgO; double sulphate of iron and ammonia corresponding to 1.8 gr. Fe_2O_3.

A pure magnesium diopside already obtained by Ebelmen is most interesting.

X. *Felspathic Meteorites.* 1 *Eukrites:* anorthite, enstatite and pyroxene; and 2, *Howardites:* anorthite and olivine, both successfully obtained.

XI. *Diabases and Dolerites with ophitic structure.* The difficulty here was to obtain elongated crystals of felspar entirely surrounded by irregular masses of homogeneous pyroxene. It was wellnigh impossible with oligoclase or labrador, whose fusing points are so near that of pyroxene. With anorthite, however, this difficulty disappears. A mixture of equal parts of both minerals subjected to temperature No. 2 four days, and as long to temperature No. 3, gave the required result. In case temperature No. 4 is used, a union of the ophitic and microlithic structure is observed in the same slide.

Experiments productive of no positive results. All attempts to reproduce rocks containing quartz, orthoclase, albite, muscovite, biotite, or amphibole by fusion have proved unsuccessful. These minerals when melted give either an amorphous glass or pass into other combinations giving rise to minerals already produced; *e. g.* hornblende changes to pyroxene.

In this way the *general important result* was obtained that the *acidic rocks*, i. e. *those containing the minerals above named, owe their origin to some other means than igneous fusion.*

G. H. WILLIAMS.

RECENT APPLICATIONS OF THE PRODUCTS OF COAL-TAR DISTILLATION.

The practical applications of the results of investigations in pure chemistry are nowhere better shown than in the utilisation of coal tar, especially in the manufacture of the almost innumerable organic coloring matters. Within recent years this branch of industrial chemistry has made enormous progress. The activity of chemists has been exerted to a much higher degree in developing the applications of the direct products of tar distillation than in bettering the methods of obtaining these products. Comparatively little improvement has been made of late in the construction of tar retorts and in the methods of tar distillation. Distillation under diminished pressure,[1] in order to obtain the high boiling compounds at a lower temperature, is gradually coming into vogue, although it leads to little or no improvement in the purity of the distillates. On the contrary, distillation with the aid of superheated or spent steam, as practised at La Villette, where the Paris gas tar is worked up, is but little used elsewhere. In recent years, several of the coal-tar hydrocarbons have found extensive practical application in the manufacture of the azo colors. The azo compounds, containing the group $-N=N-$ in combination with two aromatic nuclei, are all colored, but the azo hydrocarbons themselves have no affinity for animal and vegetable fibres, and hence cannot be used as dyes. On the other hand, such of their derivatives as contain amido or hydroxyl groups are coloring matters. Some of these have long been known, but with the exception of aniline yellow (oxalate or hydrochlorate of para-amidoazobenzene, $C_6H_5.N=N\,[1]\,C_6H_4\,[4]\,NH_2$), and Bismarck brown (hydrochlorate of triamidoazobenzene, $C_6H_4\left\{\begin{matrix}[1]\,NH_2\\ [3]\,N=N\,[1]\,C_6H_3\left\{\begin{matrix}[2]\,NH_2\\ [4]\,NH_2\end{matrix}\right.\end{matrix}\right)$ the azo compounds were not made use of until 1876. Since then, and especially since 1878, a great number of new ones have been made, many of which have been patented and manufactured on a large scale.

The oxyazo colors are made from a diazo salt and the compound of a phenol with an alkali metal, *e. g.*:

$$C_6H_5N=NCl+C_{10}H_7OK=KCl+C_6H_5N=NC_{10}H_7OH.$$

The colors may be prepared separately or developed directly upon the fabric from the appropriate substances.

The amidoazo colors are made on a large scale by the action of nitrous acid ($NaNO_2$ and HCl) on a free amine, or where this is not practicable, as when a diazoamido compound would be formed, or when a substance containing different hydrocarbon radicals is desired, by the action of a diazo salt on an amine, *e. g.*

$$C_6H_4\left\{\begin{matrix}SO_3H\\ N=NCl\end{matrix}\right.+C_{10}H_7NH_2=C_6H_4\left\{\begin{matrix}SO_3H\\ N=NC_{10}H_6NH_2HCl.\end{matrix}\right.$$

By means of these reactions the number of azo colors which may be formed from aromatic compounds containing amido and hydroxyl groups is almost infinite. When benzene and toluene were used almost solely for the production of the colors of the triphenylmethane group, the quantity obtained from gas tar was fully equal to all demands. Since the azo colors were introduced their popularity has become so great that the demand for the hydrocarbons used in their manufacture has increased greatly, and the price of these compounds is much higher than formerly. To obtain a greater supply of the hydrocarbons the attempt has been made, both in the Caucasus and in America, to make them by distilling petroleum residues through iron tubes loosely filled with bricks and heated to redness, whereby the paraffins are partially transformed into hydrocarbons of the aromatic group. This has not as yet proved a commercial success, as very extensive apparatus, requiring a large outlay of capital, is needed for working it on a large scale. It is also proposed to introduce petroleum residues into the tar retorts after the distillation is nearly completed, and then to distill again. It is, however, doubtful whether, with the ordinary tar apparatus, sufficient transformation could be obtained, especially as the separation of the aromatic hydrocarbons from the fatty hydrocarbons of nearly the same boiling points is a difficult matter. For the manufacture of azo colors practically pure benzene is required, since even small quantities of its homologues may seriously interfere with the purity of the colors. The separation of the constituents of the light oils, benzene, toluene, the xylenes, and other homologues is now almost exclusively carried on in stills like those used for distilling alcohol, consisting of a boiler provided with a vertical column many feet high, divided into compartments partially separated by horizontal partitions, and cooled by air, thus admitting of fractional condensation. By this means nearly pure products are obtained by one distillation.

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[1] Chemiker Zeitung, **3**, 146.

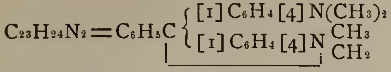
The synthesis of indigo seemed to promise a great demand for toluene. The preparation of artificial indigo, however, while offering some advantages over the use of the natural product, has not been able to compete successfully with the latter. The study of the indigo group is being vigorously carried on, and the time may not be distant when the artificial product may replace the natural as completely as artificial alizarin has replaced that extracted from madder.

At present toluene is mostly used for making rosaniline, benzoic acid, azo colors and benzaldehyde. The last is used in the preparation of the important malachite green. This color has the composition $3(C_{23}H_{24}N_2) + 2ZnCl_2 + 2H_2O$. At the works of Meister, Lucius and Brüning in Höchst, it is thus prepared: 1 mol. benzaldehyde and 2 mols. dimethylanilin are condensed by heating with zinc chloride, the reaction being

$$C_6H_5CHO + 2C_6H_5N(CH_3)_2$$

$$= H_2O + \underbrace{C_6H_5CH\left\{\begin{array}{l}[1]\,C_6H_4\,[4]\,N(CH_3)_2\\ [1]\,C_6H_4\,[4]\,N(CH_3)_2\end{array}\right.}_{\text{Tetramethyldi-p-amidotriphenylmethane.}}$$

This leuco-base, by oxidation with chloranil, loses two hydrogens, giving



$$C_{23}H_{24}N_2 = C_6H_5C\left\{\begin{array}{l}[1]\,C_6H_4\,[4]\,N(CH_3)_2 \\ [1]\,C_6H_4\,[4]\,N\begin{array}{l}CH_3\\CH_2\end{array}\end{array}\right.$$

which in combination with zinc chloride forms malachite green.

The three nitrobenzaldehydes also form condensation products with the aromatic amines by action of zinc chloride, giving various substituted nitrodiamidotriphenylmethanes, leuco-bases which either by direct oxidation or oxidation after reduction of the nitro group, yield the bases of various coloring matters. Thus paranitrobenzaldehyde and aniline give a nitrodiamidotriphenylmethane, which, after reduction of the nitro group, can be oxidised to pararosaniline. A method which would enable us to obtain paranitrobenzaldehyde cheaply and of sufficient purity would perhaps make a revolution in the methods of manufacturing the rosaniline colors.

Xylene finds application in the manufacture of certain red azo colors. The xylidine used for this purpose is made from crude nitroxylene, which is prepared from crude xylene, a mixture of o- m- and p-xylenes. Crude xylidine has also been applied recently in the synthesis of so-called cumidine, amidopseudocumene, from which azo colors are made. It is obtained by heating a mixture of crude xylidine hydrochlorate and methyl alcohol to 230° C. under pressure. Methylxylidine hydrochlorate and water are thus formed, but at this temperature, according to the principle discovered by Hofmann and Martius,[1] the methyl passes into the aromatic part of the molecule, forming amidopseudocumene. Martius has recently isolated from the crude mixture thus obtained a new crystallised cumidine, from which azo colors may be made.

Pure naphthalene is now prepared on a large scale and used for making azo colors, while formerly it was used only for making phthalic acid, which found application in the manufacture of the phthaleïn colors. The naphthalene azo colors are made from the naphthylamines and naphthols and their derivatives, especially the naphthol mono- di- and trisulphonic acids. Many of these are manufactured on a large scale, especially in Germany. Among the most important of these colors is croceïn scarlet, the sodium or sodium-ammonium salt of the compound

$$C_6H_4\left\{\begin{array}{l}[1]\,SO_3H \\ [4]\,N = N\,[1]\,C_6H_4\,[4]\,N = N\,.\,C_{10}H_5\left\{\begin{array}{l}[\alpha]\,SO_3H\\ [\beta]\,OH\end{array}\right.\end{array}\right. .$$

α-Naphthylamine is made for practical purposes by reduction of α-nitronaphthalene. β-Nitronaphthalene being unknown, the β-amine could be prepared only indirectly and with difficulty until Caro[2] obtained it by the action of ammonia on β-naphthol at 150°–160° C., some of the secondary amine being also formed.

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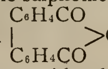
[1] Berichte der deutschen chemischen Gesellschaft, **4**, 742.

[2] *Ibid.* **14**, 1589.

About the same time Merz and Weith[1] found that by heating β-naphthol with ammonio-zinc chloride to 200°–210° C., the primary and secondary β-naphthylamines are formed, the latter, however, in much greater quantity. More recently Benz[2] has found that by using ammonio-calcium chloride, the primary amine is formed in much greater amount than the secondary amine. Benz also found that the α-amine could be similarly prepared from α-naphthol. Whether the β-amine can be practically prepared by Benz's method remains to be seen. It is not probable that his method of making the α-amine will ever replace the old method of reduction of α-nitronaphthalene.

But little progress has been made of late years either in the preparation or application of anthracene. Its quality has even degenerated rather than improved. Instead of boiling the tar down only to soft pitch, as was customary about fourteen years ago, it is now common to continue the distillation until hard pitch is obtained. While more anthracene is thus obtained, it is relatively more impure, being contaminated with larger quantities of the higher boiling hydrocarbons, from which it is separated with difficulty, and which are prejudicial to its use.

Of the innumerable compounds which exist in coal tar, the only ones which are at present extracted for practical purposes are benzene, toluene, xylene, naphthalene, anthracene, phenol and the cresols; the hydrocarbons chiefly for the color industry, and the phenols for disinfecting and antiseptic purposes. Phenol is also largely used in making salicylic and picric acids and some azo colors. Other useful ingredients of tar are at present more profitably manufactured by indirect methods.

Some of the substances occurring in abundance in tar have as yet been put to no practical use, as phenanthrene and other high boiling hydrocarbons, and carbazol. Phenanthrene, obtained as a residue in the purification of anthracene, is used for little else than making lampblack. It has also been used to replace oil in oil baths, but owing to its comparative volatility it is objectionable. Eugen Fischer[3] obtained from resorcin and phenanthrene-disulphonic acid a yellow dyestuff. Anschütz and v. Siemienski[4] have made a red azo color from diazobenzene-sulphonic acid and phenanthrol. The anhydride of diphenic acid  $\left.\begin{array}{l}C_6H_4CO\\ |\\ C_6H_4CO\end{array}\right>O$, obtained by oxidising phenanthrenequinone, forms with phenol and resorcin colored compounds analogous to the phthaleïns.[5] As yet, however, phenanthrene, although readily obtained in pure condition, has not been employed in the color industry.—(*Based upon an article in the Chemiker Zeitung*, 7, 371 *and* 387.) H. N. S.

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[1] Berichte der deutschen chemischen Gesellschaft, **13**, 1300.
[2] *Ibid.* **14**, 2344; **16**, 8. [3] *Ibid.* **13**, 314. [4] *Ibid.* **13**, 1180.
[5] Graebe and Mensching, *Ibid.* **13**, 1304.

ON THE INCONSTANCY OF THE ATOMIC WEIGHTS.

After the admirable investigations of Stas on chemical proportions it would seem almost presumptuous to call in question the accuracy of the law of definite proportions. Schützenberger,[1] in analysing the petroleum of the Caucasus, frequently obtained 101 to 101.5 per cent. of carbon and hydrogen. In seeking an explanation of this, he claims to have observed that if the petroleum, or pure benzene or aniline be distilled over sodium or copper, they acquire the property of giving more than 100 per cent. on analysis. If kept in the dark they retain it for a long time, but exposure to the light destroys this property, and, when analysed after such exposure, they gave 100 per cent. The analyses, he states, were made with the greatest care, and he is unable to account for the anomaly otherwise than by supposing that the composition of water and carbon dioxide varies within certain narrow limits, or that the atomic weights are not always constant.

Butlerow,[2] speaking of Schützenberger's observations, also regards with favor the idea that the atomic weights are variable. The atomic weights, he holds, although they cannot be expressed in whole numbers, approach in so many cases to whole numbers that it can hardly be attributed to accident. The hypothesis of Prout is, therefore, not altogether without foundation, which conclusion was also reached by Mallet and Clarke. Empirical data, from which is deduced a general law which can be expressed in a simple and rigid way, do not exactly correspond with such a law, but vary within certain limits, according to the conditions of the experiment. For example, Boyle's or Marriotte's law. Hence, Butlerow raises the question whether under certain conditions Prout's hypothesis does not actually represent the truth, and therefore concludes that on this basis the absolute constancy of the atomic weights might be denied. In a subsequent communication[3] Schützenberger mentions the observations which led him to assume that the law of definite proportions is not absolute. Barium carbonate, prepared by precipitating pure baryta water with carbon dioxide at the boiling temperature, contains, if it is first dried at 110° and then at 440°, 21.7 per cent. CO_2 and 78.5 per cent. BaO. If the carbonate is then heated in a current of oxygen to red heat it increases in weight without losing carbon dioxide; the product contains 22.0–22.05 per cent. CO_2, and 76.5 per cent. BaO. Hence barium carbonate has the power of fixing oxygen, which has increased the relative weight of carbon dioxide. Carbon monoxide was passed over a weighed quantity of copper oxide at a red heat, the carbon dioxide and reduced copper determined. The weight of copper oxide, minus the weight of the copper found, gave the weight of oxygen used, and the weight of carbon dioxide found, minus the weight of oxygen used, gave the weight of carbon monoxide consumed. The ratio CO : O was found to be 14 : 8.05, instead of 14 : 8. Hence, one equivalent of carbon monoxide can take 8.05 parts of oxygen from copper oxide. In making syntheses of water he obtained results, according to which the ratio O : H varied between 7.95 and 8.15. In other cases the variation was still greater, and as he could obtain no constant ratio he concludes that the composition of the water formed varies with the condition of the copper oxide, the length of time it is in contact with it, and temperature at which it is formed! By numerous other analyses he claims to have shown that the composition of many metallic oxides varies within certain limits which depend upon the methods of their formation.

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[1] Chemical News, **45**, 50.

[2] Journal der russ. phys. chem. Gesellsch. 1882, 208.

[3] Bull. Par. **34**, 268.

Schützenberger has not published the details of his experiments, nor given a description of his apparatus. It should be stated further that the idea of the variableness of chemical composition is not original with him. Marignac[1] in 1860 raised the same question which Schützenberger now raises, and it led Stas to carry out his admirable investigations on the laws of chemical proportions, in which, by the most accurate experimental methods, using every imaginable precaution to avoid error, he succeeded in showing that, under all conditions of temperature and pressure, bodies combine in absolutely fixed and unchangeable proportions,[2] that these proportions are real constants, that the laws of chemical combination are mathematically exact and not mere approximations which hold within certain limits. E. H. K.

NOTES.

On the Properties of Antiseptics and of the Volatile Products of Putrefaction.

M. Gustave Le Bon has recently been carrying on investigations upon the action of antiseptics, the results of which have led him to the following conclusions:

1. The disinfectant power of any antiseptic is the more feeble as the putrefaction is the more advanced. If for a normal liquid there be taken an aqueous solution containing a tenth of its weight of minced meat, this solution will exhale during the first stages of putrefaction an extremely fetid odor, which, however, can be destroyed by a comparatively small amount of antiseptic. At the end of about two months new bodies with a special odor will be

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[1] Bibliothèque universelle de Genève, **9**, 97.

[2] Stas. Chemische Proportionen, 15–108.

developed, which, contrary to what might be supposed, can only be destroyed by quantities of the same antiseptic at least twice as great as at first.

2. If the power of antiseptics be measured by taking as a means of comparison their disinfectant properties upon a given weight of the normal solution mentioned above, it will be seen that the most powerful disinfectants are potassium permanganate, "chloride of lime," sulphate of iron acidified with acetic acid, phenol, and the glyceroborates of sodium and potassium. To disinfect, for example, 10 cc. of the normal solution will require 500 cc. of a saturated aqueous solution of salicylic acid, 80 cc. of a saturated solution of phenol, 80 cc. of a ten per cent. solution of glyceroborate of sodium, and only a few drops of a one per cent. solution of potassium permanganate.

3. There is no parallelism between the disinfectant action of an antiseptic and its action upon microbes. Potassium permanganate, which is one of the most powerful disinfectants, exercises no appreciable action upon microbes. Alcohol, which on the contrary checks their development, exerts only a very feeble disinfectant action upon the products of putrefaction.

4. There is likewise no parallelism between the power of preventing putrefaction and that of checking it when it has begun. Phenol and alcohol, which are excellent preservative agents, have but a slight action upon putrefaction when it has begun, and if phenol is so useful in surgery, it is solely as a preventive agent.

5. With the exception of a very few substances which are powerful toxic agents, such as mercuric chloride, the greater number of antiseptics, and notably phenol, have only a very feeble action upon bacteria. If 10 cc. of the normal solution mentioned above be mixed with 50 or even 100 cc. of a saturated aqueous solution of phenol, the larger bacteria are made motionless, but the smaller remain in full activity, and may be perfectly reproduced by cultures. M. Le Bon even considers phenol as one of the best liquids which can be employed to preserve living bacteria for a long time.

6. The experiments made upon cadaver alkaloids cannot serve to decide the question as to whether the volatile alkaloids, which give to putrefaction its odor, are poisonous, for such experiments have generally been made by introducing into the system putrefaction products containing bacteria, to which the effects observed may be attributable. The method of experimenting adopted by M. Le Bon has been simply to place frogs in jars, in the bottom of which there is a very thin layer of the normal liquid already mentioned. Under these conditions it was noticed that at the beginning of putrefaction the liquid, although rich in sulphuretted hydrogen, possessing an extremely fetid odor, swarming with bacteria, and, as is known, very virulent if injected under the skin, had no appreciable effect upon the animals placed in the jar. On the other hand, the same liquid, two months old, and, as is

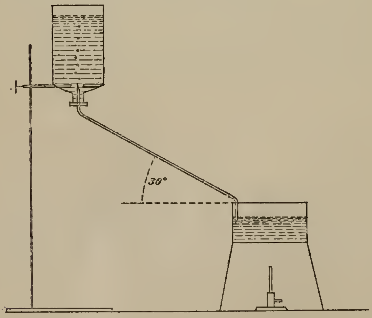
also known, no longer having virulent properties, kills in a few minutes the animals which breathe its exhalations. There is then no parallelism between the virulent power of a body in putrefaction and the toxic power of the volatile compounds which it gives off. These two properties even seem to be in inverse ratio to each other.

7. The extremely minute quantity of the products of advanced putrefaction necessary to kill an animal by simple mixture with the air which it breathes, shows that these volatile alkaloids are extremely poisonous, and experiments involuntarily made upon himself by M. Le Bon during the course of his investigations indicate that they are equally poisonous to man. M. Le Bon states that he knows of but very few bodies, such as nicotine, prussic acid, and the new alkaloid extracted by him from tobacco, which are equally poisonous.

8. The preceding experiments explain the accidents which have accompanied the exhumation of bodies interred for a long time, and prove that the atmosphere of cemeteries may, contrary to what has been stated judging by its freedom from microbes, be very dangerous. The volatile alkaloids engendered by the action of microbes upon certain organic substances play, beyond doubt, an important role in very many affections.—(*Comptes Rendus*, **95**, 259.) R. D. C.

Constant Water-Bath.

The following simple form of constant water-bath, which wastes no water, I have found to be very convenient:



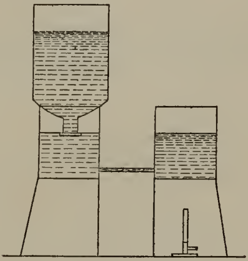
A tube of glass or metal, not less than one-quarter of an inch internal diameter, the ends of which are cut off obliquely, is bent as shown in the cut. It should make an angle of about 30° or a little greater with the horizontal. The angle may be diminished if the bore of the tube is increased. One end is inserted in the water-bath, the other in an inverted bottle. The height of the water in the bath is regulated by the depth of immersion of the tube in it. The boiling is not interrupted by the feeding, which takes place slowly and regularly. It is necessary that the ends of the tubes should be cut off obliquely. The same form of tube answers equally well for keeping a constant level in a filter or drying chamber.

A brass tube is much better than a glass one, as it does not crack at the water-level after using for a time. Brass tubes can easily be bent by ramming full of sand, stopping the ends and bending them over a curved surface. A large number of baths can be run by this apparatus by connecting them with a bath fed by it.

CHARLES T. POMEROY.

NOTE.—We have used for a number of years in this laboratory a form of constant water-bath which was contrived by Mr. Edward Bogardus, formerly chemist to the N. J. State Geological Survey. As I have not seen it described in print, and as it is cheap, simple, efficient and ingenious, I will draw attention to it here.

The following cut represents the apparatus :



It consists of two tomato cans connected by a tin tube. Into one of the cans a bottle of water is inverted. We generally use a five-pound acid bottle. The other can makes the bath. This bath can be left running over night without fear. A large number of baths can be run by this contrivance by simply connecting them by means of rubber tubes, with a reservoir replenished by an inverted bottle. Old fruit cans make excellent baths. A series of holes can be punched round the lower edge of a fruit can, thus affording a distributing reservoir. Corks holding short pieces of glass tube are inserted into the holes. By means of these the reservoir can be connected by rubber tubes with a number of baths at quite a distance. The baths are made by punching a hole near the lower edge of a fruit can and inserting a cork and short piece of glass tube. When the extra vents of the reservoir are not used they can be closed by a short rubber coupling and a pinch-cock.—[PETER T. AUSTEN, Chemical Laboratory of Rutgers College (N. J. State Scientific School).

Separation of Sugar from Molasses and Syrups by means of Strontium Saccharate formed at low temperatures.

The process here described was devised by Dr. C. Scheibler, of Berlin. If strontium hydroxide be added to a 20–25 per cent. solution of sugar at a temperature of 70–75° C. in the proportion of one molecule of $Sr(OH)_2.8H_2O$ to one molecule of $C_{12}H_{22}O_{11}$, there is formed a strongly supersaturated solution of monobasic strontium saccharate. The warm concentrated solution, if protected from the carbon dioxide of the air, and allowed to cool to ordinary temperatures, remains unchanged for some time without anything separating. It is possible to obtain either strontium hydroxide or monobasic strontium saccharate from it accordingly as we add crystals of one or the other substance to the solution. The monosaccharate by this means can be obtained in the form of a white granular powder having the composition represented by the formula $C_{12}H_{22}O_{11}SrO.5H_2O$. These facts have found practical application in a method for the extraction of sugar from molasses and syrups. The molasses whose percentage of sugar is approximately known is diluted with water and heated to boiling, a solution of strontium hydroxide of known strength is then added until for each molecule of sugar present one and a quarter molecules of $Sr(OH)_2.8H_2O$ have been added. The liquid is then allowed to cool to ordinary temperatures, and a few crystals of strontium monosaccharate added. At once the crystallisation of this compound begins and continues for 12 to 24 hours. In this way two-thirds to three-fourths of the sugar in the solution is removed. The mono-saccharate is separated from the mother-liquor in the usual way by means of filter-presses, centrifugals, etc. The strontium saccharate is then suspended in water and decomposed by carbon dioxide. After filtration there remains a solution of sugar free from strontium, from which crystallised cane sugar is obtained by evaporation.

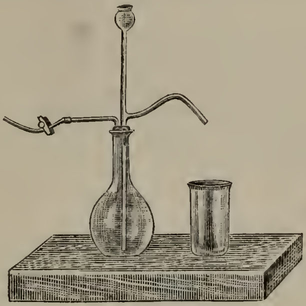
The mother-liquor separated from the crystals of monosaccharate still contains from one-fourth to one-third of the original quantity of sugar present in the molasses. To recover this the liquid is boiled for a long time with an excess of strontium hydroxide; all the sugar is thus precipitated as bibasic strontium saccharate. The liquor is decanted from the bisaccharate and the excess of strontium recovered by allowing it to cool, when a portion crystallises as strontium hydroxide; the remainder is precipitated with carbon dioxide. The residual liquid free from sugar and strontium leaves the factory to be used as a fertiliser, or is worked up for the potassium salts, ammonia, etc., which it contains.

The bibasic strontium saccharate is added to the next portion of molasses to be treated; it dissolves readily, forming monosaccharate, because of the excess of sugar present. When completely dissolved the hot concentrated solution of molasses is treated with a warm solution of strontium hydroxide of known strength, until the molecular relation between the total quantity of sugar (sugar of the molasses and sugar of the bisaccharate) is to the strontium hydroxide as 1 to 1¼. The liquid is allowed to cool and the monosaccharate separated as before. By operating in this way all the sugar in molasses or syrups may be obtained as monobasic strontium saccharate, which is easily decomposed into strontium carbonate and pure sugar.—(*Chemiker Zeitung*, 1883, **7**, 420.)

E. H. K.

A New Gas Generator.

The following apparatus I have recently devised, and as it has not, as far as I know, been heretofore described, I think it is worth a short notice. It is a rule that applies to most chemical apparatus, and especially to gas generators, that the simplest is the best, and this requirement is certainly filled by the one here described.



It consists, as is seen from the accompanying figure, of a flask fitted with a cork with two perforations. Through one of these passes an ordinary outlet tube, and through the other a funnel tube with a Y attachment. On a rubber tube leading from the outlet tube is placed a pinchcock. The material is placed in the flask, the pinchcock opened, and acid added through the funnel tube. When it is desired to stop the operation it is only necessary to close the pinchcock, when the liquid will be forced up the funnel tube, and will flow out of the curved Y attachment into a vessel placed to receive it. From this it can be poured back into the flask when desired for use. Of course it is necessary for the funnel tube to reach to the bottom of the flask; and when this is the case it will carry out very nearly the last drop of acid, thus reducing to a minimum the waste of materials and the escape of gas into the room. If desired, a round-bottom flask supported by a stand may be used, as it will cause the last drops of acid to collect at the end of the funnel tube and be carried out.

Aside from its simplicity and the ease with which it is constructed, I have found this apparatus to work more satisfactorily than the more complicated forms. It will not become clogged with ferrous sulphate when used for generating hydrogen sulphide; nor after the pinchcock is closed can the generation of gas continue, from small lumps of the solid reagent dropping into the acid, as always happens to a greater or less extent in Kipp's and similar forms of apparatus. Probably its chief advantage over most other forms is the ease with which the acid can be renewed.

J. R. DUGGAN.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, *March*, 1883.

Investigations upon the Relative Oxidability of Cast Iron, Steel, and Wrought Iron.

M. GRUNER gives the results of some long-continued experiments carried on by him upon the relative oxidability of cast iron, steel, and wrought iron, having in view the changes in rails, metallic constructions, and the hulls of vessels, by rusting and the action of sea water. It has been supposed by some engineers that this relative oxidability could be determined by submitting the different kinds of iron to the action of acidulated water. But it would be necessary to prove first that acidulated water produced the same effect as moist air or sea water, for the identity of action is not evident *a priori.*

In order to solve this question, M. Gruner made use of an apparatus consisting of a wooden framework, in which were suspended twenty-eight polished plates of steel and iron more or less hard or soft, pure or impure, each having a surface of a square decimeter. The plates were suspended by their corners 15 mm. apart, and by means of the framework could be simultaneously plunged into a bath containing acidulated water or sea water, or simply exposed to the action of moist air upon an open terrace. The plates were carefully cleaned and dried, and were weighed before and after each experiment.

The results obtained were as follows:

The experiments with moist air have not been continued long enough to decide whether the degree of carburation or the temper of the steels influenced or not the degree of corrosion by rust, and experiments upon this point are still in progress. Nevertheless the following points were determined: In twenty days the steels lost upon an average 3–4 grams per plate, the chrome steels were oxidised more, and the tungsten steels less, than the ordinary carbon steels. The cast irons were oxidised less than the steels and wrought irons, and among them the white specular iron (spiegel), containing 20 per cent. of manganese, less than the grey irons. The average loss in weight was about half that of the steels.

Sea water attacks iron, dissolving it like acidulated water, but under entirely different conditions. In a very short time chloride of iron is found in the bath. Unlike moist air, sea water attacks cast iron more strongly than steel, and white specular iron especially energetically. Thus in nine days, while the steels lost but 1–2 grams according to their nature, the white manganese iron lost 7 grams, the black iron, for the manufacture of Bessemer steel, 3.5 grams, and the phosphoric cast iron 5 grams. The tempered steels were less attacked than the annealed, and the soft steels less than those containing manganese or chromium, and tungsten steel less than ordinary steel having the same percentage of carbon. Acidulated water, like sea water, dissolves grey iron more rapidly than steel, but not the white specular iron; the impure grey iron is the most strongly attacked. Thus in three days, in a bath of water containing .5 per cent. of sulphuric acid, renewed each day, the white specular iron lost 1.5 gram, pure charcoal iron .8 gram, and the steels from 1.1 gram to 4.1 gram.

The results of these experiments show that while, as regards chromium, manganese, and tungsten, the action of acidulated water is almost the same as that of sea water, in other respects it is entirely different, and is above all totally different from the action of moist air. Experiments with acidulated water can then show nothing as regards the relative resistance of different kinds of iron to the action of moist air or of sea water.—(*Comptes Rendus*, 96, 195.) R. D. C.

On Oxidation in the Blood.

It is known that even arterial blood has scarcely more action than free oxygen on many substances which are readily oxidised when taken into the body. E. SALKOWSKI has devised a method of testing the oxidising power of blood under conditions which admit of very rapid and complete renewal of its oxygen. It consists in converting blood, to which various substances have been added, into fine spray by means of an atomiser, whereby a very large surface is exposed to the air and perfect oxygenation secured. The atomiser, holding about two and a half litres, is kept at a temperature of 40–42°, the spray being condensed in a large open cylinder and passed through the apparatus as often as desired. To make up for loss of water by evaporation, the blood is occasionally diluted with 0.6 per cent. sodium chloride solution. In the experiments described, the atomising of two or two and a half litres of blood required from one half to one hour, the process being repeated about sixteen times.

Hydrocinnamic acid (sodium salt) which is almost completely oxidised in the body to benzoic acid,[1] was recovered from the blood unchanged, no benzoic acid being detected. Benzene, which is oxidised in the body to phenol, pyrocatechin and hydroquinon,[2] though added frequently and carefully diffused, gave only traces of phenol. On the contrary, two and a half litres of blood, to which had been added two cc. of pure salicylic aldehyde, gave about .17 gram of salicylic acid, after being atomised for eight hours, although no special precaution was taken to prevent loss. A second experiment gave similar results. In two control experiments, in which blood was replaced by water containing 0.6 per cent. sodium chloride and 0.2 per cent. sodium carbonate with 2 cc. of salicylic aldehyde, and in the second also gum arabic, to increase its viscosity, only traces of salicylic acid were obtained. The experiment was not made with blood serum. The author intends to apply the same method to blood containing other compounds of the aromatic and fatty series, especially to the carbohydrates, which, according to Nencki and Sieber,[1] are oxidised in alkaline solution by free oxygen.—(*Zeitschrift für physiologische Chemie*, **7**, 115.)

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[1] Zeitschrift für physiologische Chemie, 7, 168.

[2] Reichert and Du Bois Reymond's Archiv, 1867; Zeitschrift für physiologische Chemie, 4, 336.

H. N. S.

On the liquefaction of oxygen and of nitrogen, and on the solidification of carbon bisulphide and of alcohol.

In a short note to M. Debray, MM. S. Wroblewski and K. Olszewski give some account of their experiments upon the liquefaction of oxygen and nitrogen. The memorable experiments of Cailletet and Raoul Pictet upon the liquefaction of gases indicated the possibility of reducing oxygen to the liquid state in glass tubes, as may be done with carbon dioxide, provided a sufficiently low temperature could be obtained. About a year ago Cailletet recommended liquefied ethylene as a means of producing intense cold. This liquid, under the pressure of the atmosphere, boils at —105°, as measured by a thermometer containing bisulphide of carbon. Having compressed oxygen in a tube, and cooled it by means of liquefied ethylene to —105°, Cailletet observed, when some of the gas was suddenly allowed to escape, "a tumultuous ebullition which lasted for an appreciable time, and resembled the projection of a liquid into the cooled portion of the tube," but the liquid and gas could not be separated. Profiting by the experience of Cailletet, MM. Wroblewski and Olszewski made use of a new apparatus, by means of which a comparatively large amount of gas could be placed under a pressure of several hundred atmospheres, and proceeded to study the temperatures produced by the sudden escape of gases under pressure. Their investigation very soon led them to the discovery of a temperature at which carbon bisulphide and alcohol freeze, and at which oxygen is easily and completely liquefied. This temperature is obtained by allowing liquefied ethylene to boil in a vacuum. The temperature produced by this means is dependent upon the degree of the vacuum, the lowest temperature produced up to the present being —136°, as determined by the hydrogen thermometer. The critical temperature of oxygen is lower than the boiling point of liquefied ethylene under the atmospheric pressure, which is in fact not —105°, as has been stated up to the present, but between —102° and —103° as determined by the hydrogen thermometer. According to the experiments of MM. Wroblewski and Olszewski, oxygen commences to liquefy at a pressure of 26.5 atmospheres and temperature of —131.6°. Liquid oxygen is colorless and transparent like carbon dioxide. It is very mobile and forms a sharp meniscus. Carbon bisulphide freezes at about —116° and melts at —110°. Alcohol becomes viscous like oil at about —129°, and solidifies to a white mass at —130.5° A late dispatch from M. Wroblewski to M. Debray, dated April 16, says: "Nitrogen cooled, liquefied by sudden escape, meniscus visible, liquid colorless."—(*Comptes Rendus*, **96**, 1140.) R. D. C.

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[1] Journal für praktische Chemie [2] **26**, 140.

On the Foundations of Thermo-Chemistry.

The following paragraphs are taken from an article[1] by LOTHAR MEYER:

"It cannot have escaped the unprejudiced observer, that in spite of the large number of thermo-chemical observations, and in spite of the trustworthiness of a considerable proportion of the constants deduced from them, we can as yet scarcely speak of having a knowledge of chemical transformations based upon a thermo-chemical foundation. Although individual authors have attempted to develop this subject, the majority regard their investigations with doubt and uncertainty, if not with opposition; a fact which is surprising when we consider the high and undisputed respect which the mechanical theory of heat enjoys in our time. This may indeed arise partly from the fact that many an excellent chemist, in the effort to find methods for the preparation of new coloring or colorless compounds, does not spare the time necessary to assimilate the mass of results obtained in thermo-chemical investigations. It is also possible that many a one who has studied the subject has felt the necessity of caution, in consequence of the extreme care with which the master of thermo-chemical experimentation refrains from utilising for theoretical purposes the material which he has published by the volume . . . . However this may be, the principal reason why the thermo-chemical theory has thus far made so little headway is the fact that the majority of chemists justly feel that the subject is not yet sufficiently developed. . . . .

"As we cannot deny the validity of the principal laws of the mechanical theory of heat, the source of the contradiction must be sought for in an incorrect application of them. And here indeed, in my opinion, lies the whole cause of the present uncertain and uncomfortable condition of thermo-chemistry. We bother ourselves with old worn-out hypotheses and theoretical conceptions, which physics has long ago given up, and are then surprised that the world of reality does not conform to our preconceived notions which are based upon these dogmas.

"The first of these dogmas, but one which is as yet fraught with little danger, I see in the assumption that the atoms are particles *with attractive power acting through space*, while it is quite possible, if not indeed highly probable, that everything which we call attraction is caused by certain motions of small particles, by impact or pressure. If this is also true of affinity, then the satisfying of affinity does not consist in a transformation of potential into kinetic energy, but union as well as separation of affinities are only transformations of one form of kinetic energy into another. This difference in conception is not a particularly great one, but it destroys the value of the conclusions that the separation of united affinities must necessarily be a production of *potential* energy, and that, on the contrary, a union of these affinities must be a transformation of potential into kinetic energy."

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[1] Annalen der Chemie, **218**, 1.

Molecular Weight of Haemoglobin.

Assuming that the compounds of haemoglobin (Hb) with oxygen (O_2), carbon monoxide (CO), and nitrous oxide (NO), contain 1 mol. haemoglobin to 1 mol. of gas, the molecular weight of haemoglobin can be determined if we know the exact volume of any of these gases with which a given weight of haemoglobin will combine. The attempts to determine the oxygen by dissociation of the compound HbO_2 *in vacuo* have not given concordant results, owing to the solubility of oxygen in water and the difficulty of obtaining perfect dissociation without partial decomposition of haemoglobin. By converting the compound HbO_2 into the more stable compound containing carbon monoxide and measuring the oxygen evolved, Hüfner[1] found, as the mean of ten determinations, that 1 gram haemoglobin (of the dog) combines with 1.202 cc. oxygen (0°, 1 meter pressure). MARSHALL, in Hüfner's laboratory, has recently determined the volume of carbon monoxide in the haemoglobin compound by shaking a solution containing a known weight of the compound with nitrous oxide, whereby the carbon monoxide is expelled and the compound with nitrous oxide formed. The residual gas was collected and the evolved carbon monoxide determined after removal of excess of nitrous oxide by oxygen and water. The apparatus and method employed were essentially those of Hüfner.[2] The advantage of Marshall's method consists in the comparatively great stability of the compounds of haemoglobin with carbon monoxide and with nitrous oxide, and in the slight solubility of carbon monoxide in water. Marshall finds, as the mean of ten experiments, that 1 gram of dog's haemogoblin combines with 1.205 cc. carbon monoxide (0°, 1 meter pressure), giving as the molecular weight of HbCO 14157, whence he deduces the formula:

$$C_{637}\,H_{1025}\,N_{164}\,Fe\,S_3\,O_{190}\,!$$

—(*Zeitschrift für physiologische Chemie*, **7**, 81). H. N. S.

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[1] Journal für praktische Chemie [2] **22**, 385.

[2] *Ibid.* 383.

ERRATUM.—Page 41, last line, read *nitrite* for *nitrate.*

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ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XV.—OXIDATION OF β-CYMENESULPHAMIDE.

BY IRA REMSEN AND W. C. DAY.

By the oxidation of paradiethyl-sulphamide it has been shown[1] that the group C_2H_5 is protected from the action of chromic acid by the presence of the sulphamide group. Continuing the same line of investigation, the next question to be answered was whether the complex group C_3H_7 can be, in the same way, fully protected from oxidation. We may here again refer[2] to the highly unsatisfactory experiments of von Gerichten[3] on this subject, which do not enable us to draw a definite conclusion. One of us working with L. B. Hall[4] has proved that when the sulphamide of ordinary cymene, which is known to have the sulphamide group in the ortho position relatively to methyl, and in the meta position relatively to propyl, as expressed in the formula,[5] $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_2NH_2(o)\\ C_3H_7(p)\end{array}\right.$, is oxidised with chromic acid, the methyl is protected and the propyl converted into carboxyl. What now will be the conduct of the isomeric β-cymenesulphamide in which the sulphamide group is ortho relatively to the propyl as expressed thus: $C_6H_3\left\{\begin{array}{l}C_3H_7\\ SO_2NH_2\ (o)\\ CH_3\ (p)\end{array}\right.$? In order to prepare this compound we started from cymene, introduced successively bromine and the sulphonic acid group, then extracted the bromine by means of nascent hydrogen, and converted the acid thus obtained into the corresponding sulphamide. This proved to be the β-compound as we had hoped. The amide was oxidised with chromic acid and was found to conduct itself towards chromic acid quite differently from the α-compound, the entire propyl group being protected, as had seemed at least probable.

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[1] Remsen and Noyes, this Journal, **4**, 197.

[2] For fuller reference see *loc. cit.*

[3] Berichte der deutschen chemischen Gesellschaft, **11**, 1586.

[4] Remsen and Hall, this Journal.

[5] Formulas of this kind have one great advantage over those in common use. They involve no hypothesis whatever regarding the structure of benzene. If, instead of the letters (*o*), (*p*), we use the figures (1), (3), we at once commit ourselves to some particular scheme for the representation of benzene. To say that two groups are in the ortho position to each other is quite a

Bromcymene-sulphonic Acid.

Monobromcymene was prepared according to the directions given by Landolph.[1] A little more than the required quantity of bromine was added drop by drop to the cymene. The hydrocarbon contained a few grams (4 to 5) of iodine in solution, and the retort was placed in cold water. After all the bromine had been added, the product in the retort was heated on a water-bath for some time, and a current of air was forced through the liquid to drive out, as far as possible, the hydrobromic acid and any free bromine which might be left. After treating the contents of the retort with sodium carbonate and afterwards with a little caustic soda, the product was distilled with water vapor and subjected to fractional distillation. In the vessel in which the

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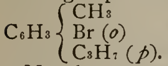
different thing from saying that the two groups are in the positions 1, 2; and the former statement is very much to be preferred. We can determine by experimental methods whether two groups are in the ortho position to each other or not, but we cannot determine whether they are in the positions 1, 2. It would be a gain if chemists would accustom themselves to use consistently such formulas as that given above. The principle, as is plain, is simply this: Let any one of the substituting atoms or groups serve as a starting-point and refer the others which may be present to this starting-point by means of the letters (*o*), (*m*) and (*p*). In some cases it will be necessary to refer a group to two others to accurately represent its relations. It is then only necessary to add a second letter indicating the relation between the group thus marked and the one above it in the formula. Thus (I) $C_6H_2\left\{\begin{array}{l}CH_3\\ Br\ (o)\\ SO_2OH\ (m)\ (o)\\ C_3H_7\ (p)\end{array}\right.$ and (II) $C_6H_2\left\{\begin{array}{l}CH_3\\ Br\ (o)\\ SO_2OH\ (m)\ (p)\\ C_3H_7\ (p)\end{array}\right.$ represent two isomeric bromcymenesulphonic acids. In (I) the sulphonic acid group is in the meta position relatively to methyl and ortho to bromine. In (II) the same group is meta to methyl, but para to bromine. Its relation to bromine is different in the two compounds, but its relations to methyl and propyl are the same. I. R.

[1] Berichte der deutschen chemischen Gesellschaft, **5**, 267.

distillation with water was carried on there remained behind a comparatively small quantity of a non-volatile, black, gummy mass, the nature of which was not determined. That which came over with the water was mainly bromcymene, which was obtained pure after a few distillations. The vapor is irritating to the eyes and nose. When perfectly pure it is colorless, but, on standing for a time, it becomes slightly colored. Its boiling point was found to be 228–229° (uncorrected) and 237° (corrected). In all we obtained about 800 grams of pure bromcymene from 1200 grams of cymene. It has been shown by von Gerichten[1] that the relations of the groups in this compound are expressed by the formula



$$C_6H_3\begin{cases} CH_3 \\ Br\ (o) \\ C_3H_7\ (p). \end{cases}$$

Monobromcymene was converted into the sulphonic acid by treating it with a mixture of ordinary concentrated sulphuric and fuming sulphuric acids. The former is not strong enough and the latter may be so strong as to char the substance. By adding the mixture cautiously and preventing the reaction from becoming too violent, perfect solution of the bromcymene can be effected, and when this solution remains clear after dilution with water the transformation is complete. The sulphuric acid solution solidifies on cooling, and consists then of a mass of crystals which have a dark purple color. On diluting with water to a sufficient extent the mass is easily dissolved. This solution was neutralised with chalk, filtered and evaporated to crystallisation. The principal product obtained in this way is a calcium salt which crystallises in long beautiful needles. It is easily soluble in hot water and much less in cold. Another salt was obtained from the last mother-liquors. This could not be obtained in crystallised form, the solution forming a thick, gummy syrup. This salt and corresponding acid have not been studied as yet. It formed but a very small proportion of the entire product.

The analyses of the well-crystallised calcium salt gave the following results:

I. 0.4790 gram salt lost 0.1069 gram H_2O at 135°
II. 0.4139 " " 0.0894 " " 125°
III. 0.3187 " " 0.0685 " " 125°
IV. 0.5028 " " 0.1055 " " 135°

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 1586.

V. 0.4299 gram salt dried at 175° gave 0.09385 gram $CaSO_4$.

VI. 0.3973 gram dried salt gave 0.0874 gram $CaSO_4$.

Calculated for $(C_{10}H_{12}BrSO_3)_2Ca + 9\frac{1}{2}H_2O$.		Found.			
		I.	II.	III.	IV.
H_2O	21.51	21.50	21.62	21.49	20.98

Calculated for $(C_{10}H_{12}BrSO_3)_2Ca$.		Found.	
		I.	II.
Ca	6.41	6.42	6.46

Barium bromcymenesulphonate, $(C_{10}H_{12}BrSO_3)_2Ba + 9\frac{1}{2}H_2O$. The free acid was prepared from the calcium salt by exactly precipitating the calcium from the solution by means of sulphuric acid. The acid was neutralised by boiling with pure barium carbonate. The salt is readily soluble in hot water, but less in cold. It crystallises like the calcium salt in long beautiful needles. It readily loses some of its water of crystallisation when exposed to the air, and hence the results of the determinations of water do not agree well with each other. In analysis I the salt was used as soon after removal from the solution as possible. In the other cases there were intervals of greater or less length between the time of exposure of the salt to the air, and that of the analysis.

I. 0.7063 gram salt lost 0.1334 gram H_2O at 130°; and gave 0.1845 gram $BaSO_4$.

II. 0.4366 gram salt lost 0.0492 gram H_2O at 130°; and gave 0.1246 gram $BaSO_4$.

III. 0.5311 gram salt lost 0.0334 gram H_2O at 145°; and gave 0.1590 gram $BaSO_4$.

IV. 0.4490 gram salt lost 0.0457 gram H_2O by standing one day in a calcium chloride desiccator, and 0.0306 gram more when heated to 145°, making a total loss in weight of 0.0763 gram; and gave 0.1203 gram $BaSO_4$.

V. 0.3727 gram salt lost 0.0549 gram H_2O at 120°; and gave 0.1013 gram $BaSO_4$.

VI. 0.3544 gram salt lost 0.0542 gram at 125°; and gave 0.0969 gram $BaSO_4$.

Calculated for $(C_{10}H_{12}BrSO_3)_2Ba + 9\frac{1}{2}H_2O$.		Found.					
		I.	II.	III.	IV.	V.	VI.
H_2O	19.17	18.88	11.26	6.28	16.99	14.73	15.29

The salt with $8H_2O$ requires 16.65 per cent.; that with $7\frac{1}{2}H_2O$, 15.77 per cent.; $7H_2O$, 14.88 per cent.; $5H_2O$, 11.10 per cent.; $3H_2O$, 6.96 per cent.

	Calculated for $(C_{10}H_{12}BrSO_3)_2Ba$.	Found. I.	II.	III.	IV.	V.	VI.
Ba	19.00	18.93	18.91	18.78	18.97	18.75	18.97

Zinc bromcymenesulphonate, $(C_{10}H_{12}BrSO_3)_2Zn + 8H_2O$. This salt was obtained from the barium salt by double decomposition with zinc sulphate. It crystallises readily in long needles. It is easily soluble in hot water; less so in cold.

I. 0.3128 gram salt lost 0.0567 gram H_2O at 150°.

	Calculated for $(C_{10}H_{12}BrSO_3)_2Zn + 8H_2O$.	Found.
H_2O	18.16	18.12

Magnesium bromcymenesulphonate $(C_{10}H_{12}BrSO_3)_2Mg + 9\frac{1}{2}H_2O$. This was obtained from the barium salt by double decomposition with magnesium sulphate. Its properties are like those of the salts above described. It crystallises in long needles and is easily soluble in hot water; less in cold.

I. 0.3498 gram salt lost 0.0769 gram H_2O at 145°; and gave 0.0477 gram $MgSO_4$.

II. 0.6225 gram salt lost 0.1357 gram H_2O at 155°; and gave 0.0944 gram $MgSO_4$.

	Calculated for $(C_{10}H_{12}BrSO_3)_2Mg + 9\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	21.95	21.98	21.79

	Calculated for $(C_{10}H_{12}BrSO_3)_2Mg$.	Found. I.	II.
Mg	3.95	3.49	3.88

Sodium bromcymenesulphonate, $C_{10}H_{12}BrSO_3Na + 4\frac{1}{2}H_2O$. The barium was precipitated by means of sodium carbonate from a solution of barium bromcymenesulphonate. The sodium salt thus obtained crystallises in fine needles, and is easily soluble in hot and cold water.

0.305 gram salt lost 0.0604 gram H_2O at 135°; and gave 0.0528 gram Na_2SO_4.

	Calculated for $C_{10}H_{12}BrSO_3Na + 4\frac{1}{2}H_2O$.	Found.
H_2O	20.46	19.80

	Calculated for $C_{10}H_{12}BrSO_3Na$.	Found.
Na	7.30	6.99

The *nickel salt* was prepared by treating a solution of the barium salt with nickel sulphate. It is easily soluble and crystallises in fine needles of a delicate green color.

Bromcymenesulphamide, $C_{10}H_{12}BrSO_2NH_2$, was prepared in the usual way from the sodium salt. It is only slightly soluble in hot water and is practically insoluble in cold water. It dissolves readily in alcohol and crystallises from a mixture of alcohol and water in fine needles. The fusing point was found to be 192° (uncorrected) and 197° (corrected).

Estimations of sulphur were made by the method of Liebig, and also by that of Fahlberg and Iles. When the Liebig method was used, the first precipitate of barium sulphate obtained was dissolved in sulphuric acid and reprecipitated.

I. 0.2076 gram amide gave 0.17168 gram $BaSO_4$.
II. 0.1933 " " 0.1557 "
III. 0.1973 " " 0.1652 "
IV. 0.1553 " " 0.1272 "

Calculated for $C_{10}H_{14}SO_2NBr$.		Found. I.	II.	III.	IV.
S	10.95	11.35	11.05	11.50	11.24

Bromcymenesulphonic acid has been previously prepared by Paterno and Colombo[1] and by Paterno and Canzoneri.[2] The former state that, when bromcymene is treated with a mixture of concentrated and fuming sulphuric acids at 100°, two crystallised sulphonic acids are formed, and that it is difficult to separate them. The latter made the acids by heating bromcymene with sulphuryl chloride, under which circumstances there are formed a bromcymenesulpho-chloride and a second bromcymenesulphonic acid which passes into solution. The amide of the acid fused at 191°, and was hence probably identical with the one obtained by us. We experienced no difficulty whatever in obtaining the main acid in pure condition and in large quantity.

β-Cymenesulphamide.

In order to replace the bromine of the bromcymene-sulphonic acid by hydrogen, a solution of the sodium salt was treated with sodium amalgam. The solution was placed in large evaporating dishes and kept liberally supplied with amalgam containing from 1.5 to 3 per cent. of sodium. The complete replacement required about two weeks for each solution containing 100 grams of the salt. The end of the operation was detected by acidifying a small portion of the solution with nitric acid and exactly precipitating the bromide with silver nitrate. The filtrate from silver bromide was evaporated to dryness and heated with pure lime. If no bromine was found by dissolving in nitric acid and adding silver nitrate, the strongly alkaline solution was neutralised with sulphuric acid, and the sodium sulphate separated as completely as possible by crystallisation. When no more sodium sulphate could thus be obtained the mother-liquors were evaporated to dryness. The residue was pulverised and heated for some time in an air-bath at 110°, then treated with an equal weight of phosphorus pentachloride. It was found to be necessary to slightly heat the mixture of salt and phosphorus pentachloride in order to complete the reaction. The mass became semi-liquid and towards the end of the operation free bromine was given off from the sodium bromide. Then the whole became nearly dry and colorless, when the reaction was complete. After cooling, the mass was treated with concentrated aqueous ammonia and allowed to remain in contact with it for ten or twelve hours. At the end of this time the solution was filtered from the amide, and the ammoniacal filtrate neutralised with hydrochloric acid, which caused the precipitation of a small quantity of dissolved amide.

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[1] Gazzetta chimica Italiana, **7**, 421.

[2] *Ibid.* **11**, 124; and Berichte der deutschen chemischen Gesellschaft, **14**, 1288.

To purify the amide it was first washed thoroughly with cold water, then dissolved in alcohol and decolorised by means of bone black. It usually contains a small quantity of a yellowish colored substance which has a low fusing point. If the amide is heated with water the colored impurity sinks to the bottom as an oil while the amide itself rises to the top of the water. By now adding alcohol cautiously the amide can be brought into solution, while the oily substance remains undissolved. From the solution in alcohol and water the amide crystallises, on cooling, in glistening scales. It is insoluble in cold water and to only a very slight extent in boiling water. It is very easily soluble in hot alcohol, and crystallises from the concentrated solution on cooling. It fuses when perfectly pure at 148° (uncorrected) and 151° (corrected). It was carefully tested for bromine and found to be entirely free from it. Estimations of sulphur and nitrogen were made with the results given below.

The first two analyses were made by Liebig's method, no special precaution being taken to remove dissolved silver. In the remaining analyses the presence of silver was prevented by a method which will be referred to in the following article.

I. 0.1642 gram amide gave 0.181 gram $BaSO_4$.
II. 0.24945 " " 0.2812 "
III. 0.3569 " " 0.3916 "
IV. 0.2138 " " 0.2304 "
V. 0.2824 " " 0.3045 "

Calculated for $C_{10}H_{12}Br.SO_2NH_2$.		Found.				
		I.	II.	III.	IV.	V.
S	15.02	15.13	15.47	15.06	14.79	14.80

The nitrogen estimations were made by the absolute method, the tube being exhausted by means of a Sprengel pump of the extremely convenient form suggested by Johnson and Jenkins.[1]

I. 0.1911 gram amide gave 11.6 cc. nitrogen at 18.8° and 759.5 mm.

II. 0.3058 gram amide gave 19 cc. nitrogen at 20° and 756 mm.

Calculated for $C_{10}H_{12}Br.SO_2NH_2$.		Found.	
		I.	II.
N	6.57	6.97	7.07

The amide obtained by us has then the composition of cymenesulphamide, and the reactions made use of are of such a kind that it is difficult to see how they could have caused a molecular rearrangement. The amide is plainly quite a different substance from *α*-cymenesulphamide. This has been thoroughly studied and its properties are well known. It fuses at 113–114°. As, according to the commonly accepted hypothesis, there can be but two sulphamide derivatives of paracymene, represented respectively by the formulas (I) $C_6H_3\left\{\begin{matrix}CH_3\\ SO_2NH_2\ (o)\\ C_3H_7\ (p)\end{matrix}\right.$ and (II) $C_6H_3\left\{\begin{matrix}C_3H_7\\ SO_2NH_2\ (o)\\ CH_3\ (p)\end{matrix}\right.$ and as the well-known *α*-amide has been proved to have the formula I, it would seem to follow that our amide fusing at 147.5°–148° must be represented by formula II. We started from cymene and introduced bromine. The product is represented by the formula $C_6H_3\left\{\begin{matrix}CH_3\\ Br\ (o)\\ C_3H_7\ (p)\end{matrix}\right.$. Into this the sulphonic acid group was introduced. On now replacing the bromine by hydrogen the product is found to be a compound of the formula $C_6H_3\left\{\begin{matrix}C_3H_7\\ SO_2OH\ (o)\\ CH_3\ (p)\end{matrix}\right.$. Hence it follows that bromcymenesulphonic acid must have the formula $C_6H_2\left\{\begin{matrix}CH_3\\ Br\ (o)\\ SO_2OH\ (m)\ (p)\\ C_3H_7\ (p)\end{matrix}\right.$ or $C_6H_2\left\{\begin{matrix}CH_3\\ Br\ (o)\\ SO_2OH\ (m)\ (o)\\ C_3H_7\ (p)\end{matrix}\right.$.

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[1] This Journal, 2, 28.

Earlier investigators have described a β-cymenesulphonic acid supposed to have the formula $C_6H_3\left\{\begin{matrix}C_3H_7\\ SO_2OH\ (o)\\ CH_3\ (p)\end{matrix}\right.$, but the properties of the amide obtained from this acid are not like those of our amide. Thus Claus and Cratz[1] refer to a second acid formed when cymene is treated with sulphuric acid. Later, Claus[2] gives directions for the preparation of β-cymenesulphonic acid. The best yield is obtained by treating one part of pure cymene with five parts of concentrated sulphuric acid for from six to eight hours on the water-bath, the mixture being frequently shaken. Several salts of the acid were prepared, as well as the chloride and amide. Of the amide he only says that it was obtained in the form of an uncrystalline oil. Either it was very impure or it was entirely different from our product. Spica[3] also claims to have obtained β-cymenesulphonic acid, but if his statement is correct that the amide of the acid fuses at 73.5°–74°, then it is clear that his product was not identical with ours. According to later statements by Spica[4] and by Claus[5] it seems possible that the amide first obtained by Spica and described by him as β-cymenesulphamide is in reality a derivative of metacymene, which, according to Spica,[6] is contained in cymene from camphor.

Notwithstanding the fact that our amide has the composition of cymenesulphamide and was prepared by reactions which can leave little doubt in regard to its nature, it must be considered an open question whether it is really β-cymenesulphamide. The mere fact that its properties are not the same as those of the β-cymenesulphamide of Claus is not sufficient to arouse serious doubt in our minds concerning its nature, for it is quite possible that further investigation of the β-cymenesulphonic acid obtained directly from cymene may show it to yield an amide identical with ours. Other facts, however, which have been developed in the course of this investigation, and which will be more fully described in the next paper, seem to be inexplicable if our amide is really β-cymenesulphamide in which the propyl group is normal.

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[1] Berichte der deutschen chemischen Gesellschaft, **13**, 901. [2] *Ibid.* **14**, 2139. [3] *Ibid.* 652.

[4] *Ibid.* **15**, 791, and Gazzetta chimica Italiana, **12**, 482.

[5] Berichte der deutschen chemischen Gesellschaft, **15**, 1015. [6] *Loc. cit.*

The transformation of the amide into thymol would be of some assistance in attempting to solve the problem.

Fusion of β-Cymenesulphamide with Potassium Hydroxide.

A few grams of β-cymene sulphamide were fused with potassium hydroxide. A dark colored oil soon separated on the surface of the fused mass, and the odor of thymol was at once perceived. This odor continued throughout the fusion, the oil disappearing very slowly. On cooling, the oil solidified and proved to be mainly unchanged sulphamide. The contents of the crucible were dissolved in water and acidified, when the odors of sulphur dioxide and of thymol became very distinct. The solution was extracted with ether and the ether distilled off. There remained behind a crystalline mass of dark color which had the unmistakable odor of thymol. It was impossible to distinguish between the odor of this substance and that of pure thymol. Nevertheless, we were unable, with the small quantity at our disposal, to isolate the pure thymol. While in our minds there is little, if any, doubt that thymol was thus obtained synthetically, we can furnish no perfectly satisfactory proof. If we consider the very strong and characteristic odor of thymol, however, it must be acknowledged that proof based upon recognition of this odor is fairly convincing.

The conversion of the sulphamide into the corresponding hydroxyl derivative does not take place very readily at a low temperature, and, if the temperature be raised much higher, deeper decomposition takes place. We hope to return to this subject at some future time.

Oxidation of β-Cymenesulphamide.

The best proportions for the oxidation of the amide we have found to be: 5 grams amide to 25 grams potassium pyrochromate, 40 grams concentrated sulphuric acid diluted with three times its volume of water. The mixture was boiled for six hours in a flask connected with an inverted condenser. After cooling, the contents of the flask were diluted with water, filtered and washed until the wash-water passed through colorless. The white crystalline acid upon the filter was dissolved in a dilute solution of sodium carbonate. The solution was filtered and allowed to stand, when some unchanged amide crystallised out. On adding hydrochloric acid a precipitate was formed, which after filtering and washing was converted into the barium salt. This is extremely soluble. Its solution was evaporated down to a small volume and allowed to stand, when a small quantity of unchanged amide again separated. The acid was set free, washed, filtered, crystallised from water, and again converted into the barium salt. This process was repeated several times, as it was extremely difficult to completely remove the small quantity of amide. Finally, however, the acid was obtained in perfectly pure form. It is comparatively easily soluble in hot water, and crystallises, on cooling, in the form of beautiful, long needles. It fuses at 232° (uncorrected) and 244° (corrected). Sulphur and nitrogen estimations were made with the following results:

I. 0.2344 gram substance gave 0.227 gram $BaSO_4$.

II. 0.4164 gram substance gave 23 cc. nitrogen. Temperature 30°C.; pressure 758 mm. Absolute method with mercury pump.

Calculated for $C_{10}H_{13}O_4SN$.		Found.
S	13.17	13.30
N	5.76	5.98

Analyses of the barium salt were also made. Analyses (I), (II), (III) and (IV) were made with specimens of the salt which we afterward found to contain small quantities of unchanged amide, and from which it was finally separated by the method described above. Analyses (V) and (VI) were made with the perfectly pure substance.

I. 0.2273 gram salt lost 0.0179 gram H_2O at 125°; and gave 0.0767 gram $BaSO_4$.

II. 0.2504 gram salt lost 0.0217 gram H_2O at 150°; and gave 0.0842 gram $BaSO_4$.

III. 0.2912 gram salt lost 0.0265 gram H_2O at 148°; and gave 0.0973 gram $BaSO_4$.

IV. 0.2410 gram salt lost 0.0219 gram H_2O at 150°; and gave 0.0808 gram $BaSO_4$.

V. 0.3173 gram salt lost 0.0198 gram H_2O at 154°; and gave 0.1115 gram $BaSO_4$.

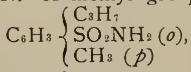
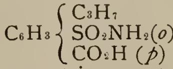
VI. 0.4685 gram salt lost 0.0324 gram H_2O at 154°; and gave 0.1637 gram $BaSO_4$.

The results for water of crystallisation do not agree well with one another. It is probable that the first specimens analysed (I–IV) were not perfectly dry. They were poorly crystallised, while the two pure specimens (V and VI) were much better crystallised.

	Calculated for $(C_{10}H_{12}SO_4N)_2Ba + 3H_2O$.	Found.			
		I.	II.	III.	IV.
H_2O	8.00	7.87	8.66	9.10	9.08

	Calculated for $(C_{10}H_{12}SO_4N)_2Ba + 2\frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	6.74	6.24	6.91

	Calculated for $(C_{10}H_{12}SO_4N)_2Ba$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Ba	22.06	21.53	21.64	21.61	21.68	22.03	22.07

Discarding the results of the first four analyses for the reasons above given, it will be seen that the agreement between the calculated and found percentages for barium is almost perfect. It follows that the acid with which we are here dealing has the composition $C_{10}H_{13}SO_4N$. The amide which yields this acid by oxidation has the composition $C_{10}H_{15}SO_2N$. A methyl group is changed to carboxyl. From the amide,  $C_6H_3\left\{\begin{array}{l} C_3H_7 \\ SO_2NH_2\ (o) \\ CH_3\ (p) \end{array}\right.$, we have obtained by oxidation the acid,  $C_6H_3\left\{\begin{array}{l} C_3H_7 \\ SO_2NH_2 (o) \\ CO_2H\ (p) \end{array}\right.$, *i. e. sulphamineparapropylbenzoic acid.* The most important point to be noted in this connection is the fact that the entire propyl group, C_3H_7, is protected from the action of the oxidising mixture—a fact which is in perfect harmony with the views which were advanced some time ago by one of us, and the correctness of which is being more and more satisfactorily demonstrated by the investigations carried on in this laboratory. In fact, the conduct of the two cymenesulphamides towards chromic acid furnishes the most striking illustration of the working of the law of protection. The α-amide, $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_2NH_2\ (o)\\ C_3H_7\ (p)\end{array}\right.$, yields sulphamine-paratoluic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_2NH_2(o)\\ CO_2H\ (p)\end{array}\right.$. In this case, the methyl being in the ortho position relatively to the sulphamide group, is protected, while the propyl group breaks down and yields carboxyl, exactly as if the sulphamide group were not present. In the case of the β-amide, however, as has been seen, the propyl group being now in the ortho position relatively to methyl, is protected, while the methyl is changed to carboxyl. This is certainly the simplest interpretation of the reactions which have been considered in this paper, and were it not for facts established in an investigation which was carried on by Mr. E. H. Keiser and one of us simultaneously with this, there would be no good reason for thinking that anything had taken place besides that which appears at first sight. As will be pointed out, however, it seems at least possible that the normal propyl group of cymene may have undergone a change to the isopropyl group under the influence of some of the reagents used. It would, however, be premature to discuss this possibility without having first considered the unexpected facts which have suggested it.

Whether the group in our amide be normal propyl or isopropyl, and this is the only question in regard to the compound which can be considered open, the fact remains that the entire group is protected, and the main object in view as well as the result obtained are not in the least affected by the possible transformation.

XVI.—OXIDATION OF PARA-DIPROPYL-BENZENE-SULPHAMIDE.

By Ira Remsen and E. H. Keiser.

The object of this investigation was like that of the one just described—to determine whether an acid group in the ortho position relatively to propyl has the power to protect this group from the oxidising action of chromic acid. In this case we started from paradipropylbenzene, introducing into it the sulphonic acid group and transforming the acid into the corresponding amide. According to all that we know of the compound thus prepared, it must contain the sulphamide group in the ortho position relatively to one propyl group, and in the meta position relatively to the other. In the light of the results described in the preceding paper we would expect such a compound to yield by oxidation a sulphamine-para-propyl-benzoic acid identical with the one described above. As will be seen, an acid of the composition of a sulphamine-parapropylbenzoic acid was actually obtained in this case as well as the other; but, strange to say, the two have quite different properties.

Paradipropylbenzène was prepared according to the directions given by Körner.[1] Eighteen flasks of 125 cc. capacity were charged each with 25 grams paradibrombenzene, 39 grams propyl bromide (from Kahlbaum, boiling point 71°), 14.6 grams metallic sodium cut in thin shavings, and 10 grams pure benzene. Each flask, provided with a long glass tube to serve as a condenser, was placed in a vessel containing cold water and allowed to stand until the action seemed to be finished. To each flask there was then added 10 grams propyl bromide, after which it was heated in an oil bath for two hours at 120°. To prevent loss there was attached a condenser with a mercury valve. The flask was then heated over a naked flame and everything volatile distilled off. The distillate thus obtained was fractioned and the dipropylbenzene easily obtained in pure condition. From the eighteen flasks, containing 450 grams dibrombenzene, we obtained 86 grams of the hydrocarbon boiling between 210° and 220°. By far the greater part of this passed over at 214° (uncorrected) or 224° (corrected). Körner gives the boiling point at 220°–222°.

Para-dipropyl-benzene-sulphonic Acid.

To about 75 cc. of fuming sulphuric acid 40–50 grams of the hydrocarbon were gradually added, the flask being constantly shaken. The mixture became warm at once, and the reaction was easily completed by heating the substances on a water-bath for a few minutes. After diluting, the acid was neutralised with barium carbonate. The barium salt of the sulphonic acid crystallised out of the concentrated solution in the form of minute needles, which effloresced rapidly in the air. Analyses gave the following results:

I. 0.2885 gram salt lost 0.0086 gram H_2O at 160°, and gave 0.1032 gram $BaSO_4$.

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[1] Annalen der Chemie, **216**, 223.

II. 0.4515 gram salt lost 0.0147 gram H_2O, and gave 0.1633 gram $BaSO_4$.

III. 0.1876 gram lost 0.007 gram H_2O.

Calculated for $(C_{12}H_{17}SO_3)_2Ba + 2H_2O$.		Found.		
		I.	II.	III.
H_2O	5.49	2.98	3.25	3.78

Calculated for $(C_{12}H_{17}SO_3)_2Ba$.		Found.	
		I.	II.
Ba	22.13	21.68	21.98

The barium salt was converted into the potassium salt by treatment with potassium carbonate. It crystallises in large transparent plates, which retain their transparency after the water of crystallisation is driven off.

0.3174 gram salt lost 0.0072 gram H_2O at 140°, and gave 0.0955 gram K_2SO_4.

Calculated for $(C_{12}H_{17}SO_3)K + 4H_2O$.		Found.
H_2O	2.04	2.26

Calculated for $(C_{12}H_{17}SO_3)K$.		Found.
K	13.95	13.82

To convert the potassium salt into the amide it was treated in the usual way successively with phosphorus pentachloride and strong aqueous ammonia. Ammonia gas was passed into the liquid for some time to insure the perfect transformation of the chloride into the amide. The amide is difficultly soluble in boiling water; easily soluble in alcohol. When pure it fuses at 103°, and if allowed to solidify suddenly it will melt again at a lower temperature. From the alcoholic solution it may be obtained in the form of perfectly clear transparent crystals. These appear to be monoclinic prisms, and at times they reach a length of at least half an inch. Very perfect, clear rhombohedra were afterwards obtained. At our request, Dr. G. H. Williams has examined the crystals and reports as follows regarding them:

"The crystals of paradipropylsulphamide intrusted to me by Prof. Remsen for examination, though at the first glance appearing to consist of a monoclinic combination, ∞P (110) and $0P$ (001), proved to belong to the rhombohedral division of the hexagonal system. The examination of a large number of crystals failed to reveal any other form than the fundamental rhombohedron, R, which is generally so much elongated in the direction of one zone of combination edges as to give the crystals an acicular habit. Sometimes the rhombohedron is developed in the form of a thin plate parallel to one of the faces, and then generally has a hopper-like shape characteristic of crystals whose growth has been rapid. More rarely, among the minutest crystals, symmetrically developed rhombohedrons were observed. The crystals were all quite small, very seldom exceeding 4 mm. in length by 1 mm. in thickness.

"The average of measurements on five crystals gave for the rhombohedral angles 104° 27′ 54″ and 75° 29′ 12″, the agreement being as great as could be expected, considering the somewhat uneven character of the planes. The axial ratio calculated from these angles is $a : c = 1 : 0.85592$, showing a close similarity to that of calcite (= 1 : 0.8542988).

"In parallel polarised light all crystals extinguish parallel to the diagonals of the rhombohedral faces. In converged light a uniaxial interference figure with a large number of rings, indicating a great divergence of the two rays, as in the case of calcite, was observed. Double refraction negative.

"On account of the minuteness of the crystals, and still more on account of the extreme brittleness of the substance, it was found impossible to prepare sections perpendicular to the vertical axis or prisms for the determination of the index of refraction.

"In all crystallographic as well as optical properties the close resemblance of this substance to calcite is very striking."

Estimations of sulphur and nitrogen were made. In the sulphur estimation, which was made according to Liebig's method, special precautions were taken to remove silver from the solution. This is quite necessary in order that satisfactory results may be obtained. One of us (K.) has undertaken a study of the best conditions for the estimation of sulphur in organic compounds.[1] The results obtained are very satisfactory.

I. 0.2464 gram substance gave 0.2399 gram $BaSO_4$.

II. 0.2667 gram substance gave 13.4 cc. N at 18° and 766 mm. pressure (= 0.0156 gram N). Absolute method with Sprengel pump.

	Calculated for $C_{12}H_{19}NSO_2$.	Found.
S	13.27	13.37
N	5.81	5.85

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[1] See paper on "Estimation of Sulphur in Organic Compounds" in this number.

Oxidation of Para-dipropyl-benzene-sulphamide.

The proportions used in the oxidation experiments were these: 10 grams amide, 66 grams potassium pyrochromate and 96 grams concentrated sulphuric acid diluted with three times its volume of water. The oxidising mixture was allowed to become cold before the amide was added. The whole was boiled for from eight to ten hours. Some unchanged amide still remained in the flask, and, after cooling, formed a film on the surface of the oxidising mixture, while small crystals of the oxidation product were observed in the liquid. The liquid was filtered, leaving the crystallised oxidation product on the filter, while the cake of amide remained in the flask. The oxidising mixture was returned to the flask, and the boiling started again. When the mixture had become dark green, a few grams of the pyrochromate and a little sulphuric acid were added, and the oxidation continued until, on cooling, there was seen no film of unchanged amide on the surface of the liquid. The oxidation was effected with considerably more difficulty than that of β-cymenesulphamide as described in the preceding article. The product left on the filter was washed with cold water until the wash-water passed through colorless. It was then dissolved in boiling water and filtered, when, on cooling, it crystallised out in beautiful, long, lustrous needles. After two or three crystallisations from water it was perfectly free from the original amide. It was then found to fuse at 212°–213° (corrected). It is an acid. Its composition was determined by estimations of sulphur and nitrogen and by analyses of the barium, calcium, copper and silver salts.

The sulphur and nitrogen estimations gave the following results:

I. 0.2599 gram gave 13.3 cc. N at 20° and 761 mm. pressure (=0.0153478 gram N). Absolute method with Sprengel pump.

II. 0.2852 gram gave 0.2773 gram $BaSO_4$.

Calculated for $C_{10}H_{13}SNO_4$.		Found.
N	5.76	5.90
S	13.17	13.35

The acid has the composition of *sulphamine-propyl-benzoic acid*, and the analyses of the salts confirm these results.

Barium sulphamine-propyl-benzoate, $(C_{10}H_{12}SNO_4)Ba + xH_2O$. This salt was prepared by boiling the free acid with pure barium carbonate. It is very easily soluble and was not obtained in the form of crystals. The solution was evaporated to dryness and the salt heated to 150°.

I. 0.0975 gram dried salt gave 0.0367 gram $BaSO_4$.

II. 0.1424 gram dried salt gave 0.0533 gram $BaSO_4$.

Calculated for $(C_{10}H_{12}SO_4N)_2Ba$.		Found.	
		I.	II.
Ba	22.06	22.13	22.00

Calcium sulphamine-propyl-benzoate, $(C_{10}H_{12}SO_4N)_2Ca+6H_2O$, was prepared like the barium salt. It is very easily soluble in water and in alcohol and could not be obtained in the form of well-defined crystals.

0.2431 gram salt lost 0.0426 gram H_2O at 140°; and gave 0.0508 gram $CaSO_4$.

Calculated for $(C_{10}H_{12}SO_4N)_2Ca + 6H_2O$.		Found.
H_2O	17.09	17.52

Calculated for $(C_{10}H_{12}SO_4N)_2Ca$.		Found.
Ca	7.63	7.45

Copper Salt.—When an aqueous solution of the acid is boiled with an excess of copper oxide, the solution filtered and evaporated to a small volume, a salt separates in the form of minute blue crystals which appeared to be as easily soluble in cold water as in hot. The analyses showed it to consist of a molecule of the neutral copper salt plus a molecule of the free acid. That the compound still had acid properties was shown by dissolving a little in water and testing the solution with blue litmus paper. The addition of a little sodium carbonate to it caused an evolution of carbon dioxide. The substance had a definite crystalline form and could not for a moment be regarded as a mixture. We give the analytical results and the simplest formula deducible from them, which is $(C_{10}H_{12}SO_4N)_2Cu + C_{10}H_{13}SO_4N + 2H_2O$.

I. 0.2270 gram salt lost 0.0103 gram H_2O, and gave 0.0214 gram CuO.

II. 0.1970 gram salt lost 0.0093 gram H_2O, and gave 0.0188 gram CuO.

Calculated for the above formula.		Found.	
		I.	II.
H_2O	4.36	4.54	4.72

Calculated for dried salt.		Found.	
		I.	II.
Cu	7.97	7.87	7.98

Silver sulphamine-propyl-benzoate, $(C_{10}H_{12}SO_4N)Ag$, was prepared by adding silver nitrate to a solution of the neutral ammonium salt. It is thrown down as a flocculent white mass, which rapidly becomes brown if exposed to the light. The specimen analysed was kept in the dark until dry. The salt passes into solution in water if boiled for some time, but it does not crystallise from the solution, even when evaporated down to a small volume.

0.2732 gram dried salt gave a residue of metallic silver weighing 0.084 gram.

Calculated for $(C_{10}H_{12}SO_4N)Ag$.		Found.
Ag	30.86	30.75

It is clear from the analyses above quoted that the acid with which we are dealing has the composition of a sulphamine-propyl-benzoic acid, $C_6H_3\left\{\begin{array}{l}C_3H_7\\SO_2NH_2.\\CO_2H\end{array}\right.$ Further, as we started from para-dipropyl-benzene, the carboxyl in the acid must be in the para position relatively to the propyl. Hence the sulphamide group must be either ortho to propyl and meta carboxyl, or ortho to carboxyl and meta to methyl. Considering the results obtained in the earlier investigations of this series, we can scarcely be in doubt regarding the relation of the groups. We can see no reason why the sulphamide group should not exert a protective action upon the ortho propyl group in this case as well as in the case of β-cymene-sulphamide. But if it does exert this action, then the product obtained by oxidising para-dipropyl-benzene-sulphamide, $C_6H_3\left\{\begin{array}{l}C_3H_7\\SO_3NH_2\ (o)\\C_3H_7\ (p)\end{array}\right.$, ought to be identical with that obtained by oxidising β-cymene-sulphamide, $C_6H_3\left\{\begin{array}{l}C_3H_7\\SO_2NH_2\ (o)\\CH_3\ (p)\end{array}\right.$. It should be $C_6H_3\left\{\begin{array}{l}C_3H_7\\SO_2NH_2\ (o)\\CO_2H\ (p)\end{array}\right.$. The products obtained in the two cases are, however, not identical in properties, though they have the same composition. The sulphamine-propyl-benzoic acid obtained from β-cymene-sulphamide, and which we will hence call the β-acid, fuses at 244° (corrected), whereas the acid described in this paper, and which may be called the α-acid, fuses at 212°–213° (corrected). They resemble each other in appearance and in other general properties. Between their barium salts differences could easily be detected. That of the β-acid, although very easily soluble, could be obtained in definite crystallised form, while that of the α-acid could not be obtained in crystallised form.

How shall we explain the difference between the two acids? Without further experiments this is impossible. There are two thoughts, however, which suggest themselves and indicate the lines of work, the following of which will be most likely to lead to a solution of the curious problem which is here presented. The first is this: It is possible that in the reactions made use of for the preparation of β-cymene-sulphamide there may have been a transformation of the normal propyl into the isopropyl group, so that the final product may be an isopropyl instead of a normal propyl compound. The possibility of such a transformation has been proved in a number of cases. We recall here the following, as bearing particularly upon our own work: Kekulé and Schrotter[1] found that by long boiling of normal propyl bromide with aluminium bromide, isopropyl bromide is produced. Aronstein[2] found that this same change is effected without the presence of aluminium bromide by simply heating to 280°. Gustavson[3] has found that cymene is decomposed by bromine in the presence of aluminium chloride, yielding pentabromtoluene and *isopropyl bromide*. The same chemist has also observed[4] that cumene (isopropylbenzene) can be obtained by the action of propyl bromide on benzene in the presence of aluminium bromide. By boiling cuminic alcohol with zinc dust, Kraut[5] obtained cymene, isopropyl being in this case changed to normal propyl. Other transformations of normal propyl into isopropyl, or *vice versa*, have been observed by R. Meyer and H. Bauer,[6] Jacobsen,[7] Nencki and Ziegler,[8] Ziegler,[9] and Paterno and Spica.[10] Whether such a transformation has taken place in either of the cases under immediate consideration can probably be decided by starting from para-isopropyl-benzene and performing the same experiments as those which have been described in this paper. The product of the oxidation of the sulphamide should be identical either with the α- or the β-acid.

The second thought which has suggested itself by way of explanation of the facts with which we are dealing is that, in the preparation of β-cymene-sulphonic acid by treating bromcymenesulphonic acid with sodium amalgam, some of the nascent hydrogen may have been added to the compound, and that the product really obtained was not cymene-sulphonic acid but a hydrogen addition product. As is well known, the action of sodium amalgam in alkaline solution is made use of for the purpose of making dihydrophthalic and dihydroterephthalic acids. The presence of the two hydrogen atoms in the cymenesulphamide and in the acid obtained from it could hardly be detected with certainty by analyses. On the other hand, the great stability of β-sulphamine-propyl-benzoic acid towards the chromic acid mixture would seem to be an argument against the view that the acid is a hydrogen addition product.

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[1] Berichte der deutschen chemischen Gesellschaft, **12**, 2279.

[2] *Ibid.* **14**, 607; and Receuil des Travaux chimiques des Pays Bas, **1**, 134.

[3] Berichte der deutschen chemischen Gesellschaft, **10**, 1101.

[4] *Ibid.* **11**, 1251.

[5] *Ibid.* **11**, 1379.

[6] *Ibid.* **14**, 1135.

[7] *Ibid.* **12**, 429 and 1512.

[8] *Ibid.* **5**, 749.

[9] *Ibid.* **14**, 1144.

[10] *Ibid.* **12**, 2366.

An experiment was made in the hope of throwing some light on the question by treating the α-sulphamine-propyl-benzoic acid with sodium amalgam in alkaline solution. It was thought possible that in this way the α-acid might be converted into the β-acid. The experiment led to no positive results. We had only half a gram of substance at our disposal. This was dissolved in caustic soda, and the solution kept supplied with sodium amalgam for about three weeks. For some reason, however, we were unable to recover any of the acid unchanged, nor could we isolate any difficultly soluble substance from the solution.

As we had found the sulphamide of dipropyl-benzene to resist the action of chromic acid very markedly, it was necessary to show that, when dipropyl-benzene itself is oxidised, both propyl groups are changed to carboxyl. For this purpose, 5 grams of the hydrocarbon were treated with 33 grams potassium pyrochromate and 48 grams of sulphuric acid diluted in the usual way. The mixture was kept boiling for several hours, when the unoxidised hydrocarbon was distilled off with water. The residue was filtered, and in the filter there was collected a considerable quantity of a white insoluble powder. This was dissolved in ammonia and precipitated by means of hydrochloric acid. After drying, an attempt was made to determine its fusing point. It was found, however, that it sublimed without fusing. Its conduct showed beyond a question that it was terephthalic acid.

Finally, the oxidising mixtures filtered off from α-sulphamine-propyl-benzoic acid were evaporated down. After standing for some time a small quantity of minute white crystals separated. These were filtered off and recrystallised from water containing hydrochloric acid. They proved to be a potassium salt. When pure, the salt crystallised in needles.

The analyses gave the following results:

0.1702 gram lost 0.0063 gram H_2O, and gave 0.05 gram K_2SO_4.

These results correspond to 3.70 per cent. H_2O and 13.68 per cent. K. The salts $C_6H_3\left\{\begin{matrix}C_3H_7\\SO_2OK\\CO_2H\end{matrix}\right.$ and $C_6H_3\left\{\begin{matrix}CO_2H\\SO_2OK\\CO_2H\end{matrix}\right.$ contain almost identically the same percentages of potassium, there being a difference of only two in the molecular weights of the two substances. A neutralisation experiment showed, however, that the salt under examination still contains two replaceable hydrogen atoms.

0.1737 gram salt dried at 240° lost 0.0072 gram H_2O, and then required for neutralisation 0.02008 gram ammonia. If it had been the salt with one carboxyl it would have required 0.01003 gram ammonia, while if it is the substance $C_6H_3\left\{\begin{matrix}CO_2H\\SO_2OK\\CO_2H\end{matrix}\right.$, it would require 0.01993 gram ammonia.

Calculated for $C_6H_3\left\{\begin{matrix}CO_2H\\SO_3K\\CO_2H\end{matrix}\right. + \frac{1}{2}H_2O.$		Found. I.	Found. II.
$\frac{1}{2}H_2O$	3.10	4.14	3.70

Calculated for anhydrous salt,		Found.
K	13.76	13.68

The substance is therefore *mono-potassium sulphoterephthalate*, and it has been formed by further oxidation of either sulphopropylbenzoic or sulphamine-propyl-benzoic acid. The results obtained in estimating the water of crystallisation are not satisfactory, more than one per cent. too much having been found in the first analysis. A mono-potassium sulphoterephthalate has already been described by Remsen and Hall[1] and Remsen and Burney.[2] The properties of the substance obtained in this investigation are apparently the same as those previously ascribed to the salt. The only difference is in the water of crystallisation. In the earlier in-investigations the crystallised salt was found to contain one molecule of water. Now, however, although more than half a molecule is found, there is not as much as there ought to be. We are at present unable to explain this discrepancy.

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[1] This Journal, 2, 56.

[2] *Ibid.* 2, 412.

It is clear then that when para-dipropyl-benzene-sulphamide is oxidised by means of chromic acid, the principal product is the acid which we have called α-sulphamine-propyl-benzoic acid, the formation of which under the conditions described proves that the sulphamide group exerts a protective action upon one of the propyl groups. At the same time the protection is not perfect, as has been shown in other cases, and as is shown in this case by the formation of sulpho-terephthalic acid. In oxidising α-metaxylene-sulphamide with chromic acid Remsen and Iles[1] observed a similar formation of a small quantity of sulpho-isophthalic acid.

SYNTHETICAL RESEARCHES IN THE GLUCOSIDE GROUP.[2]

II.

By Arthur Michael.

Action of Acetic Anhydride on Phenolglucoside.

The action of acetochlorhydrose on an alcoholic solution of sodium phenyl oxide unexpectedly gave phenolglucoside, instead of the tetra-acetyl derivative of that compound. This result seemed to indicate that the tetra-acetyl compound would be decomposed in the cold by alcohol into ethyl acetate and the glucoside. The formation of helicin from acetochlorhydrose and sodium salicylaldehyde, however, showed that this conclusion can hardly be accepted, since tetra-acetyl helicin, once formed, is but slightly decomposed by alcohol, even on boiling.[3] The following experiments show that the acetyl derivative of phenolglucoside is also stable towards alcohol. To prepare the acetyl compound, a mixture of 1 part of phenolglucoside, 5 parts of acetic anhydride and 2 parts of fused sodium acetate was heated for about three hours in a hot water-bath. The product of the reaction was poured into cold water, allowed to stand for several hours, then slightly warmed and, after

[1] This Journal, **1**, 121. [2] See this Journal, **1**, 304. [3] Annalen der Chemie, **154**, 23.

cooling, filtered. The crystalline, insoluble residue was purified by two crystallisations from alcohol. On analysis the following numbers were obtained:

0.2255 gram of substance, dried at 100°, gave 0.4693 gram of CO_2 and 0.121 gram of H_2O.

	Theory for $C_6H_7O(OC_6H_5)(OC_2H_3O)_4$.	Found.
C	56.60	56.75
H	5.66	5.96

Tetra-acetylphenolglucoside crystallises from alcohol in white, glittering, long needles. It is insoluble in cold, but slightly in hot water. Cold alcohol dissolves it slightly, warm very readily. Heated with caustic soda it is decomposed into sodium acetate, sodium phenyl oxide and brown decomposition products of dextrose. It may be crystallised from hot alcohol without undergoing any noticeable decomposition. If the alcoholic solution is boiled for several minutes, the odor of ethyl acetete is noticeable. The decomposition is however very slight, for an alcoholic solution heated for an hour in a flask connected with an inverted cooler gave on cooling almost the original amount of the acetyl compound. The substance does not reduce a solution of potassium copper tartrate, except after long boiling; a reduction doubtless owing to the previous formation of dextrose.

Synthesis of Salicin from synthetical Helicin.

N. Lisenko[1] has shown that helicin obtained from salicin can be reconverted into the latter compound by treating an aqueous solution of it with sodium amalgam. This, according to H. Schiff,[2] can also be effected by using zinc and sulphuric acid. I deemed the repetition of this experiment, using helicin obtained from acetchlorhydrose and sodium salicylaldehyde, of some interest.

The directions given by Lisenko were closely followed. The aqueous solution was treated with sodium amalgam, and care was taken to keep the solution but slightly alkaline. The filtrate from the mercury was neutralised by carbonic acid, evaporated to dryness on a water-bath, and the residue extracted with hot alcohol. The reduction product was purified by several crystallisations from water. An analysis gave the following numbers:

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[1] Zeitschrift für Chemie, 1864, 577.

[2] Annalen der Chemie, **154**, 26.

0.1858 gram of substance gave 0.3706 gram of CO_2 and 0.1077 gram of H_2O.

Theory for $C_6H_{11}O_5—O—C_6H_4CH_2OH$.		Found.
C	54.54	54.39
H	6.29	6.44

The properties of the compound confirm the conclusion that may be drawn from the analysis. They agree perfectly with those of natural salicin. This is the first known instance of a synthesis of a glucoside occurring in nature.

Action of Acetochlorhydrose on Dipotassium Salicylate.

Tiemann and Reimer[1] have examined the action of potassium permanganate on salicin with a view of converting the formyl of the salicylaldehyde radical into carboxyl. The alkaline solution of the oxidation product did not change Fehling's solution, even on boiling, nor was salicylic acid precipitated on the addition of acids. If, however, the acidified solution was gently heated, on cooling salicylic acid was precipitated. This result indicated that the glucoside of salicylic acid was formed, but it was found impossible to isolate the compound in a pure state. It seemed possible to obtain this compound by the action of acetochlorhydrose on dipotassium salicylate. The investigation of the reaction gave an unexpected result. A solution of 10 parts of dipotassium salicylate, $C_6H_4OKCOOK$, and 34.5 parts of acetochlorhydrose in absolute alcohol was allowed to stand in the cold. After a short time a separation of potassium chloride began and continued for several hours. The solution was filtered, and deposited, on standing several days, clusters of needles. It is advisable to let the solution stand at least for ten days, as a separation of needles has been observed even after standing for that length of time. A better yield was obtained by allowing the filtrate from potassium chloride in a beaker to evaporate on the air. The needles were separated by filtration, washed well with alcohol, then with water, and crystallised several times from hot alcohol.

I. 0.2405 gram of substance, dried at 100°, gave 0.4720 gram CO_2 and 0.1208 gram H_2O.

II. 0.2725 gram of substance, dried at 100°, gave 0.5382 gram CO_2 and 0.1300 gram H_2O.

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[1] Berichte der deutschen chemischen Gesellschaft, **8**, 515.

Theory for $C_6H_{11}O_5—O—C_6H_4COOH$.		$C_{26}H_{30}O_{15}$.	Found. I.	Found. II.
C	52.00	53.61	53.52	53.86
H	5.33	5.15	5.58	5.30

These results show conclusively that the glucoside of salicylic acid is not the direct product of the reaction. The substance formed stands in the relation of an ether or an anhydride to that compound:

$$2C_6H_{11}O_5—O—C_6H_4COOH—H_2O = C_{26}H_{30}O_{15}.$$

It crystallises from alcohol in long, white needles, melting at 184–185°. They are insoluble in cold, sparingly in hot water; in cold alcohol slightly, they are easily soluble in warm alcohol. The aqueous or alcoholic solutions do not reduce Fehling's solution. Cold aqueous ammonia is without action; even if allowed to stand with it for several days the needles do not go into solution. When they are boiled for a long time with aqueous ammonia a gradual solution is effected. This solution reduced Fehling's solution, and also ammoniacal silver solution. A cold solution of caustic potash dissolves the substance very slowly in the cold; when heated it dissolves it easily. These solutions, heated to boiling, reduce Fehling's solution; and the addition of acids gave a precipitate of salicylic acid. In the filtrate the presence of dextrose was proved. The solution, made in the cold, does not reduce Fehling's solution, easily when heated with it. The substance is also decomposed into salicylic acid and dextrose by boiling with dilute acids. It is evident that the alkaline solution contained a glucoside of salicylic acid. The addition of acids to a very concentrated alkaline solution and extraction with ether gave a product consisting of salicylic acid and probably its glucoside, but several attempts to obtain the last substance in a pure state were fruitless.

The insolubility of the substance in aqueous ammonia proves that it does not contain carboxyl. This would seem to indicate that the substance is an anhydride of salicylic glucoside, a view which is corroborated by the investigation of its acetyl derivative. To prepare that compound the substance was heated in a water-bath with an excess of acetic anhydride and an equal weight of fused sodium acetate. The product of the reaction was boiled out with water, and the residue crystallised from alcohol. It forms long, white needles, which are insoluble in water, soluble in hot alcohol. They melt at 110°–111°. It is insoluble in caustic potash; heated with it for some time it is decomposed into potassium acetate and salicylate, and dextrose. An analysis gave the following numbers:

0.2305 gram of substance, dried at 100°, gave 0.4658 gram of CO_2 and 0.1102 gram of H_2O.

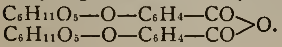
	Theory for $C_{26}O_{15}H_{24}(C_2H_3O)_6$.	$C_{26}O_{15}H_{23}(C_2H_3O)_7$.	$C_{26}O_{15}H_{22}(C_2H_3O)_8$.	Found.
C	54.67	54.81	54.90	55.12
H	5.03	5.02	5.01	5.31

Although the carbon percentage obtained in the analysis agrees better with that of an octo-acetyl derivative than with those of derivatives containing a less number of acetyl groups, still the percentages of carbon in the various possible acetyl products approximate each other too closely that the results of the analysis should determine with any certainty the number of hydroxyls in the substance. An attempt to decompose the glucoside with $\frac{1}{10}$ standard sodium hydrate and titration gave no results, on account of the decomposition of the liberated dextrose by the alkali. More satisfactory results were obtained by decomposing the substance with dilute sulphuric acid and titration with alkali. The substance was heated in a closed tube with 10 cc. $\frac{1}{10}$ standard sulphuric acid for several hours at 120°, and the contents of the tube titrated with $\frac{1}{20}$ standard potassium hydrate. The liquid was colored slightly brown, which rendered the observation of the point of neutralisation difficult. There is, however, no greater uncertainty in the readings than 0.5 cc. of the alkaline solution.

I. 0.3615 gram of substance required 97.5 cc. $\frac{1}{20}$ standard KOH.
II. 0.5182 " " " 131.8 cc. " " "

	Theory for $C_{26}O_{15}H_{23}(C_2H_3O)_7$.	$C_{26}O_{15}H_{22}(C_2H_3O)_8$.	Found. I.	Found. II.
CH_3CO	34.24	37.47	36.7	37.0

These results are strong evidence for the existence of eight hydroxyls in the compound. It is probably the anhydride of salicylic glucoside, and may be represented by



$$\left.\begin{array}{l}C_6H_{11}O_5—O—C_6H_4—CO\\C_6H_{11}O_5—O—C_6H_4—CO\end{array}\right>O.$$

The formation of such a compound from acetochlorhydrose and dipotassium salicylate is difficult to understand; and, although the properties of the substance agree with those indicated by this constitutional formula, the question as to its constitution may still be considered open.

Synthesis of Methylarbutin.

Arbutin was supposed to be the glucoside of hydroquinone, having the formula $C_{12}H_{16}O_7$, until Hlasiwetz and Habermann[1] showed that when decomposed by acids a mixture of hydroquinone and methylhydroquinone in equivalent proportions was formed. These chemists changed the formula into $C_{25}H_{34}O_{14}$. Fittig,[2] somewhat later, called attention to the probability that natural arbutin is a mixture of the glucosides of hydro- and methylhydroquinone, and H. Schiff[3] endeavored to separate the natural product by fractional crystallisation into these compounds. Pure methylhydroquinone glucoside was not obtained, but his results led him to conclude that the melting point of methylarbutin is in the neighborhood of 142°. In my first paper[4] I had already called attention to the desirability of examining the action of acetochlorhydrose on the potassium derivatives of hydro- and methylhydroquinone, with the view of settling the constitution of natural arbutin. From methylhydroquinone[5] a glucoside melting at 168°–169°, and with about the same properties as arbutin, was obtained. Lately,[6] Schiff has also obtained pure methylarbutin by the action of methyliodide and potassium hydrate on arbutin, and found its melting point to be 175°–176°.

An attempt to obtain hydroquinone glucoside synthetically gave no result. Hydroquinone dissolved in absolute alcohol gave a yellow solution on addition of sodium ethyl oxide. Acetochlorhydrose acted readily on this solution, forming acetic ether and sodium chloride, but from the filtrate a definite compound could not be obtained. Unsuccessful were also the experiments to isolate the monosodium derivative of hydroquinone. The yellow alcoholic solution gave on addition of ether a brown precipitate. This precipitate contained sodium, and gave hydroquinone when treated with acids; but it was only sparingly soluble in alcohol, and decomposed easily on exposure to the air, forming benzoquinone.

The experiments with methylhydroquinone gave more satisfactory results. This compound was prepared from arbutin (melting at 168°–169°) according to the directions given by Hlasiwetz and Habermann. To prepare the potassium derivative[7] pure potassium hydrate was dissolved in absolute alcohol, the greater part of the alcohol evaporated and an equivalent of methylhydroquinone, also dissolved in a small quantity of absolute alcohol, added. This solution was mixed with 15–20 times its volume of anhydrous ether, which precipitated the potassium compound as a white crystalline powder. It was separated as much as possible by decantation, brought on a filter, washed with absolute alcohol, and dried *in vacuo* over sulphuric acid.

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[1] Annalen der Chemie, **177**, 342.

[2] Organische Chemie, 10 Aufl. 638.

[3] Annalen der Chemie, **206**, 166.

[4] This Journal, **1**, 312.

[5] Berichte der deutschen chemischen Gesellschaft, **14**, 2100.

[6] *Ibid.* **15**, 1844.

[7] Körner and Bertoni, Berichte der deutschen chemischen Gesellschaft, **14**, 847.

0.315 gram of potassium compound gave 0.1709 gram of K_2SO_4.

	Theory for $C_6H_4\genfrac{}{}{0pt}{}{OK}{OCH_3}$.	Found.
K	24.12	24.36

If the alcohol or ether used in the preparation of the potassium compound was not free of water, a part of the substance separated as an oil, which soon solidified to large, nacreous scales. This is probably an hydrate of the above compound. Both of the compounds are soluble in alcohol and water.

To an absolute alcoholic solution of the potassium derivative (1.1 parts), acetochlorhydrose (2.5 parts) was added, and the solution allowed to stand for several days. The clear solution soon deposited potassium chloride, and the odor of acetic ether was distinctly noticeable. It was then filtered, and the filtrate allowed to evaporate by exposure to the air. When a slight excess of the potassium compound was used the crystallisation began after the liquid had stood several days, otherwise not until a week, or often even longer. The crystals were well pressed between bibulous paper, dissolved in a small amount of hot water, filtered, and the filtrate placed over sulphuric acid in a closed vessel. The crystallisation took place very slowly, more rapidly if the sides of the vessel were occasionally rubbed with a glass rod. For analysis the substance was again crystallised from water.

I. .2548 gram of substance, dried at 120°, gave 0.5066 gram of CO_2 and 0.1532 gram of H_2O.

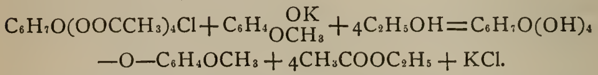
II. 0.2186 gram of substance, dried at 120°, gave 0.4354 gram of CO_2 and 0.1293 gram of H_2O.

	Theory for $C_6H_{11}O_6—O—C_6H_4OCH_3$.	Found.	
		I.	II.
C	54.54	54.23	54.32
H	6.29	6.67	6.57

The glucoside contains water of crystallisation; 0.347 gram of substance, which had stood for several weeks on the air, lost 0.120 when heated to 120°.[1]

	Theory for $2(C_{13}H_{18}O_7)H_2O$.	Found.
H_2O	3.05	3.45

The substance has the empirical formula of methylarbutin. Its formation from acetochlorhydrose and potassium methylhydroquinone is represented as follows:



$$C_6H_7O(OOCCH_3)_4Cl + C_6H_4{}^{OK}_{OCH_3} + 4C_2H_5OH = C_6H_7O(OH)_4 -O-C_6H_4OCH_3 + 4CH_3COOC_2H_5 + KCl.$$

It crystallises from water in long, colorless, silky needles, which are concentrically grouped, and have a bitter taste. They melt at 168–169° and solidify again at 137–138°. Unlike arbutin, the solidified substance melted again at 168–169°. The substance is easily soluble in alcohol and water, insoluble in ether. The aqueous solution is not precipitated by basic lead acetate, nor by copper salts; it does not reduce Fehling's solution on heating. The aqueous solution is not colored blue by the addition of dilute aqueous iron trichloride. Digested with dilute mineral acids it is rapidly decomposed into dextrose and methylhydroquinone. This decomposition may also be effected by subjecting the aqueous solution to the action of emulsin. Concentrated nitric acid dissolves the glucoside to form a yellow solution, which, when boiled with alcohol and a small amount of sulphuric acid, then diluted with water, gave a violet color on addition of potassium hydrate. The aqueous solution heated with dilute sulphuric acid and manganese dioxide gave off the penetrating odor of benzoquinone.

A comparison of the properties of synthetical methylarbutin with those of arbutin shows that but in one respect a noticeable difference occurs. While an aqueous solution of arbutin is colored blue on addition of iron trichloride, that of the methyl compound remains unchanged. This property of arbutin is undoubtedly due to the presence of hydroxyl in the aromatic radical, and is therefore due to the presence of arbutin in the natural glucoside. In methylarbutin an hydroxyl in the aromatic radical does not exist, and its behavior towards the iron trichloride solution is in accordance with its constitution, since only those aromatic compounds containing that group show this property. It is evident from the similarity in the properties of arbutin and methylarbutin that a mechanical separation could only be effected with difficulty. H. Schiff,[1] who attempted the separation by repeated crystallisations from water, obtained a product melting at 142°, which he supposed to be nearly pure methylarbutin. Recently[2] he has shown that a mixture of two equivalents of arbutin and one of methylarbutin show the same melting point, and that methylarbutin itself melts at 175–176°.[3] It may be safely inferred from the results of Schiff's and my own experiments that natural arbutin is a mixture of hydroquinone and methylhydroquinone glucosides in variable proportions.

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[1] The percentage of water is somewhat high for the formula. It is possible that the substance loses part of its water of crystallisation by long standing on the air. When analysed no change in weight was noticed in 24 hours.

Remarks on the Constitution of Salicin and Arbutin.

In my first paper[4] attention was directed to the fact that the stability of helicin towards easily reducible metallic oxides is not in accordance with its constitutional formula, according to which it contains the formyl of dextrose. On the other hand, the synthesis of helicin from acetochlorhydrose and C_6H_4OKCHO, showed almost beyond a doubt that, whatever the constitution of dextrose might be, helicin is an ether of it and salicylaldehyde. Later,[5] the suggestion was made that possibly in the oxidation of dextrose in alkaline solution by metallic oxides, the oxidation began at one of the carbinol groups of dextrose, and not as generally accepted at the formyl.[6] If in place of the hydrogen of the hydroxyl where the oxidation begins, a stable radical is substituted, a greater stability of the new product seems probable. Some observations have recently become known that make the existence of a formyl group in dextrose doubtful. Breuer and Zincke[1] have shown that benzoyl and acetylcarbinol in alkaline solution reduce copper oxide, forming phenylhydroxyacetic and lactic acids. They concluded, in their first paper, from these facts that the reducing property of dextrose may be owing to the presence of $CO—CH_2OH$. These chemists attempted to explain the above facts by assuming the decomposition of the compounds in benzoic, acetic and formic aldehydes, and then by the reuniting of benzoic and acetic aldehydes with formic aldehyde the formation of the aldehydes of phenylhydroxyacetic and lactic acids. V. Meyer[2] considers the conversion of the carbonyl-carbinols into hydroxy-acids as perfectly analogous with the oxidation of dextrose into gluconic acid, and explains the reaction by assuming that it is due to action of water and the oxygen of the oxide: $R—CO—CH_2OH + H_2O + O = R—CHOH—COOH + H_2O$. I have explained this reaction[3] in a somewhat different manner. According to it the copper oxide converts the carbinol group into formyl, and then the alkali acts, as on all aromatic aldehydes, oxidising and reducing:

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[1] Annalen der Chemie, **206**, 166.

[2] Berichte der deutschen chemischen Gesellschaft, **15**, 1842.

[3] Schiff has called attention to the differences between the melting points and water of crystallisation in synthetical and natural methylarbutin. The melting point of salicin, one of the best examined glucosides, has lately been corrected from 198° to 204°: an imperceptible amount of impurity seems to lower considerably the melting points of the glucosides. In regard to the water of crystallisation, arbutin seems to have the property of crystallising with different amounts under slightly different conditions. Although I do not think there is the least doubt as to the identity of the two methylarbutins, I will prepare both products and carefully compare their properties.

[4] This Journal, **1**, 304, 311.

[5] Berichte der deutschen chemischen Gesellschaft, **14**, 2101.

[6] H. Kiliani sees in the stability of potassium gluconate and saccharate towards Fehling's solution a proof that the reduction is due to the presence of formyl. (Berichte der deutschen chemischen Gesellscheft, **14**, 2529.) Phthalic acid is readily oxidised by potassium permanganate, whereas sodium phthalate in presence of an alkali is very stable towards that oxidising agent. (Weith, Berichte der deutschen chemischen Gesellschaft, **7**, 1058.) This shows that the effect of replacing the hydrogen of the carboxyl is to strengthen the affinity of the carboxyl to the carbon atom it is united with. It is evident that no conclusion can be strictly drawn from a difference in the behavior of the alkaline salt of gluconic acid and an alkaline solution of dextrose. Hlasiwetz and Habermann used gluconic acid, and this may be the reason of the difference between their observations and those of Kiliani.

$$C_6H_5—CO—CHO + KOH = C_6H_5—CHOH—COOK.$$

V. Meyer in comparing the formation of gluconic acid from dextrose with that of phenylhydroxyacetic acid from benzoylcarbinol overlooked a very important fact, to which attention was called in my note. Under the same conditions that dextrose goes over into saccharic acid, oxidation in acid solution (nitric acid), benzoylcarbinol does not give the hydroxy-acid, but benzoic and benzoyl formic acids. Breuer and Zincke's results might be accepted as a proof of the presence of carbonyl in dextrose, if an acid containing it were obtained by oxidation with nitric acid; as the facts now stand their experiments may be given as a proof that dextrose does not contain that radical. Zincke's view as to a previous decomposition into benzoic and formic aldehydes is difficult to understand. Formic aldehyde is extremely easily decomposed by alkalies, besides being equally easily oxidisable by metallic oxides. A second hypothesis, which he considers possible, is represented by: $C_6H_5—CO—CH_2OH + H_2O = C_6H_5—C(OH)_2CH_2OH + O = C_6H_5—CHOH—COOH + H_2O$. The formation of an acid from an aldehyde indicates pretty clearly what takes place when the oxidation occurs, it consists of the introduction of oxygen between the C and H atoms. How will Zincke explain the conversion of an alcohol into an aldehyde? Again, that nascent hydrogen should reduce the group $C(OH)_2$ to CHOH in presence of an easily reducible metallic oxide appears somewhat doubtful. The object of assuming the previous formation of the compound $C_6H_5—C(OH)_2—CH_2OH$ is also difficult to understand. If the reaction is due to the liberation of nascent hydrogen by copper oxide, surely there are good reasons for believing that a CO group is more easily reducible than a $C(OH)_2$ group.[1]

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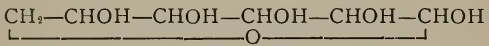
[1] Berichte der deutschen chemischen Gesellschaft, **13**, 635; Annalen der Chemie, **216**, 311.

[2] Berichte der deutschen chemischen Gesellschaft, **13**, 2344.

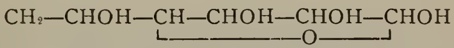
[3] *Ibid.* **14**, 2100.

Of greater importance is the observation of V. Meyer and J. G. Schmidt that dextrose does not give the aldehyde reaction with fuchsine-sulphurous acid. B. Tollens, in the last number of the German Chemical Society Journal,[2] has proposed the two following formulae for dextrose:



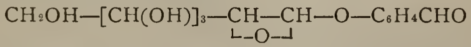
$$\underbrace{CH_2—CHOH—CHOH—CHOH—CHOH—CHOH}_{O}$$

or



$$CH_2—CHOH—\underbrace{CH—CHOH—CHOH—CHOH}_{O}$$

The first formula seems doubtful, as it is known that condensation is not likely to take place between two groups separated by six carbon atoms. The second appears to me to be the most satisfactory representation of the constitution of dextrose as yet proposed, although there is no certainty as to which of the secondary carbinol groups condense to help form the oxide.[3] In previous papers[4] I called attention that the formula



$$CH_2OH—[CH(OH)]_3—\underbrace{CH—CH}_{O}—O—C_6H_4CHO$$

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[1] Zincke (Annalen der Chemie, **216**, 315) also repeats, two years later, substantially the view given in my note, with the remark "Die Bildung dieses Aldehyds setzt auch Michael voraus." It is impossible, at present, to decide whether the aldehyde is acted upon by water and then the alkali unites with the acid formed, or whether the reduction and oxidation are caused by the direct action of the alkali, but it is certain that under the above conditions the presence of the alkali is indispensable. A similar reaction has, to my knowledge, never been observed in acid nor in aqueous solutions.

[2] **16**, 923.

[3] From gluconic and saccharic acids the formation of lactones has not been noticed, although these compounds have an hydroxyl in the gamma position to the carboxyl. It is evident that conclusions drawn from the properties of mono-hydroxy acids when applied to the above class of compounds must be accepted with caution.

[4] Berichte, **14**, 2100; **15**, 1924.

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was much better in accordance with the properties of helicin than that assuming the existence of the formyl of dextrose. Attention was also directed to the fact that such a compound could on decomposition by acids give dextrose, considered as containing formyl. In view of the observations of Schmidt regarding dextrose, it seems to me that the above, or a similar formula differing only in regard to which of the secondary carbinol groups take part in the condensation, best represents our present knowledge of the constitution of helicin. The same may be said to apply to the constitutional formulae of salicin, methylarbutin and probably most of the glucosides. In regard to salicin the following experiment is strongly confirmatory of the non-existence of formyl in it. Salicin was dissolved in alcohol and treated for several days with sodium amalgam. Care was taken to prevent the solution becoming very alkaline by addition of acetic acid. It was found that the salicin remained unchanged, whereas under these conditions dextrose is converted into mannite.

TUFTS COLLEGE, *May 12th*, 1883.

ON THE FORMATION OF CROTONIC AND β-OXYBUTYRIC ALDEHYDES FROM ETHYL ALDEHYDE.[1]

BY ARTHUR MICHAEL AND ADOLPH KOPP.

Among the many important contributions which have been made of late years to organic chemistry, few have attracted and merited more attention from chemists than synthesis by dehydration. The interest felt in this class of reactions is in no small measure due to the belief that they play a prominent role in some of the most important of all syntheses occurring in vegetable nature, the formation of carbohydrates from carbonic acid and water. The suggestion that dextrose may be formed by the dehydration of an hypothetical hydrate of formic aldehyde, and that from it the vari-

[1] The experiments described below were made in December, 1878, in the chemical laboratory of the École de Médecine in Paris. A preliminary notice is found in the Bulletin de la Société chimique (1879) **31**, 434, and also in the Berichte der deutschen chemischen Gesellschaft, **12**, 2091. The research has not attained the completeness which we had hoped to give it; but, as it is improbable that we shall together ever be able to resume work on it, we consider it advisable to publish it in its unfinished state.

ous other carbohydrates are formed, was first made by Baeyer; while Kekulé, deducing from the interesting results of his investigation on the condensation products of ethyl aldehyde, also called attention to the probability of similar reactions occurring in nature. However, not only in these views, but in the whole theory of synthesis by dehydration, there was such an element of uncertainty and improbability that the famous research of A. Wurtz on the formation of aldol from ethyl aldehyde may be considered as the beginning of a new epoch in this department of chemistry. The distinguished French chemist concluded, in view of the formation of aldol by the action of chlorhydric acid on ethyl aldehyde in the cold, it was probable that the formation of crotonic aldehyde by chlorhydric acid in the heat was preceded by that of β-oxybutyric aldehyde. Crotonic aldehyde has been obtained, not only by the action of chlorhydric acid, but by zinc chloride and several other salts, whereas the formation of aldol has not been observed in their action on ethyl aldehyde. Moreover, in Wurtz's experiments a considerable quantity of acid was used; while it has been found that a small quantity of acid or zinc chloride was able to form a large amount of crotonic aldehyde. If Wurtz's view as to the previous formation of β-oxybutyric aldehyde is capable of generalisation, in all cases when the formation of crotonic aldehyde has been observed, only proper conditions, the previous formation of β-oxybutyric aldehyde should be provable. The following experiments were made with this object, and also to ascertain whether salts which occur in vegetable nature have the property of carbon-polymerising[1] ethyl aldehyde.

Before describing these experiments, we shall give a brief review of what had been done on the subject up to the time when we published a preliminary notice, which gave the principal results of the investigation. The formation of crotonic aldehyde from ethyl aldehyde was first noticed by Wurtz and Bauer[2] and Lieben,[3] the former chemists obtaining it by the action of zinc chloride on ethylene alcohol and aldehyde, the latter by the action of concentrated solutions of potassium formate, sodium acetate, and sodium potassium tartrate at 100° on ethyl aldehyde. This chemist gave crotonic aldehyde its correct empirical formula. Our knowledge of the constitution of crotonic aldehyde is principally due to the important investigation of Kekulé,[1] who, by oxidising it to solid crotonic acid, proved it to be the aldehyde of that acid. This experiment characterised it as a butyl derivative, a view previously suggested by Baeyer.[2] The action of sodium and zinc on ethyl aldehyde has been studied by J. Riban,[3] who obtained β-oxybutyric aldehyde and the compound $C_6H_{10}O_2$ as products of the reaction. The behavior of isoamylaldehyde towards heat, sodium, and caustic potash had been previously studied by A. Borodin.[4] He obtained by the action of heat and sodium condensation-products of the aldehyde; by the action of the alkali, polymeric products that decomposed on distillation into the original aldehyde. The action of potassium carbonate in the cold gave Borodin's polymeride, while in the heat condensation-products are formed.[5] A somewhat different observation was made by Bruylant,[6] who obtained in the same reaction a solid polymeric aldehyde, while the above chemists obtained liquid products. This compound likewise decomposed into isoamylaldehyde on heating. Simultaneously with our investigation, F. Urech[7] examined the action of potassium carbonate on isobutyl aldehyde. In the cold a polymeride was formed that decomposed on heating, partially into isobutylaldehyde, in part into condensation-products of that compound. In the heat only the latter products were formed.

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[1] Carbon-polymerisation is used in this paper when the polymeride is formed by linking of carbon to carbon; oxygen-polymerisation when it is due to the linking of oxygen atoms. β-Oxybutyric aldehyde is an example of the first, paraldehyde of the second class.

[2] Comptes rendus, **51**, 55.

[3] Annalen der Chemie, Suppl. **1**, 114.

Action of Zinc Chloride on Ethyl Aldehyde.

The experiments of Kekulé on the action of zinc chloride on ethyl aldehyde are of special interest. He observed that a very small amount of zinc chloride sufficed to cause the formation of a considerable quantity of crotonic aldehyde, and that this even took place in presence of water. Kekulé's method for the preparation of crotonic aldehyde is to heat the mixture at 100°, and then distill. These are conditions under which β-oxybutyric aldehyde decomposes into crotonic aldehyde and water. In the following experiments the products of the reaction were separated under conditions permitting the isolation of the oxyaldehyde.

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[1] Annalen der Chemie, **162**, 77.

[2] Annalen der Chemie, Suppl. **5**, 81.

[3] Bulletin de la Société chimique, **18**, 63.

[4] Berichte der deutschen chemischen Gesellschaft, **2**, 552; **3**, 423; **5**, 481; **6**, 982.

[5] Gäss and Hell, Berichte, **8**, 369.

[6] *Ibid.* **8**, 415.

[7] *Ibid.* **12**, 191, 1745.

I. A sealed tube containing pure ethyl aldehyde, several drops of water, and a very small quantity of zinc chloride was heated for 24 hours at 90°. The contents of the tube, which had the penetrating odor of crotonic aldehyde, was brought into a boiling-flask and distilled under a pressure of 25 mm. The fraction passing over between 80°–120° dissolved almost entirely in water. The solution was filtered, and evaporated *in vacuo* over sulphuric acid. A thick liquid was obtained, which showed all the properties of β-oxybutyric aldehyde, and decomposed on distillation into crotonic aldehyde and water.

II. It seemed probable that in the above experiment, owing to the continued action of heat, a part of the oxyaldehyde had decomposed into crotonic aldehyde. A second tube, prepared like the first, was heated for twelve hours. The contents of this tube had but a faint odor of crotonic aldehyde. It was distilled *in vacuo*, the fraction between 80°–130° again distilled, and that portion passing over between 90°–110° dissolved in water, filtered, and the solution evaporated *in vacuo*. On analysis the following numbers were obtained:

0.6283 gram of liquid gave 1.2435 gram of CO_2 and 0.5629 gram of H_2O.

	Theory for $CH_3—CHOH—CH_2—CHO$.	Found.
C	54.54	53.97
H	9.09	8.96

The liquid was β-oxybutyric aldehyde. On long standing it thickened, and finally solidified to the para-compound.

III. The formation of oxybutyric aldehyde takes place in the cold, though very slowly. A tube, prepared as the above, was allowed to stand for ten days at 20°, and was then found to contain a small quantity of aldol.

IV. Par-aldehyde, in aqueous solution, is not converted in the cold into aldol. After the mixture was heated for ten hours at 100° the formation of aldol was proved. It is probable that the formation of aldol is due to the decomposition of par-aldehyde into aldehyde by the action of heat.

These experiments show conclusively that the first product of the action of zinc chloride on ethyl aldehyde is β-oxybutyric aldehyde and not crotonic aldehyde.[1] With this proof Kekulé's elaborate hypothesis on the function of zinc chloride in this reaction becomes superfluous. In fact, the assumption of the existence of anhydrous molecules of zinc chloride in its aqueous solution, and their preferring to dehydrate ethyl aldehyde in order to get water, instead of uniting with water already formed, was sufficient to make his views extremely improbable at the time of their publication. It is possible, as Kekulé has suggested, that the action of zinc chloride may be due to the presence of free chlorhydric acid in its aqueous solution; but, whether it be due to presence of free acid or to zinc chloride, our knowledge of the functions of these substances in the aldol formation may be said to be limited to bare facts.[1]

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[1] We made several experiments on the action of zinc chloride on a mixture of chloral and ethyl aldehyde. The mixture allowed to stand for some hours at about 30° became very thick.

Action of Potassium Salts on Ethyl Aldehyde.

Lieben, in his research on the action of weak affinities on ethyl aldehyde, examined the action of concentrated solutions of potassium formate and sodium acetate, and obtained crotonic aldehyde. We repeated his experiments, with a view of proving the previous formation of aldol. A solution of ethyl aldehyde in concentrated aqueous potassium formate heated in a sealed tube at 100° gradually divided into two layers, the upper consisting of a thick yellow oil, which increased in viscidity with continued heating. This oil has, according to Lieben, the composition of crotonic aldehyde, and yields it on distillation. It certainly contained that substance mixed with higher condensation products, and, probably, compounds that decompose into crotonic aldehyde on distillation. If

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On distillation *in vacuo* a heavy oily liquid passed over between 120°–125°, which was insoluble in water. When heated under ordinary pressure it gave off chloral and aldehyde; even when distilled *in vacuo* a slight decomposition into these products was noticed. The analyses of different preparations showed that a definite product cannot be obtained by distillation ($Cl = 47.73$; 38.76; 42.88; $C = 27.97$; $H = 3.45$). The compound is probably an oxygen-polymeride of chloral and ethyl aldehyde. If the mixture of chloral and aldehyde is heated at 100° a violent reaction ensues, resulting in a complete decomposition of the substance used.

[1] Experiments which have recently been made in the chemical laboratory of Tufts College put the function of acids in an analogous reaction, the action of aromatic aldehydes on phenols, in an entirely new light. Baeyer in most of his experiments used a considerable quantity of concentrated acids, ostensibly for the purpose of dehydration. There is no connection between the affinity of the acids for water and the reaction. To take a special case, a mixture of one part of resorcin and one part of benzoic aldehyde dissolved in two parts alcohol, is converted by the merest trace of chlorhydric acid—the temperature of the mixture rises to about 60°—quantitatively into an amorphous compound, $C_{26}H_{20}O_4$. The further action of acids, no matter how dilute, on this resin, is to convert it into a mixture of two crystalline compounds, one of which is isomeric with it. This compound has all the properties of a crystallisable resin, and undoubtedly belongs to that group. A full account of the investigation will appear in an early number of this Journal. A. MICHAEL.

aldol were formed it should be found in the aqueous layer. This was extracted with ether and the extract distilled *in vacuo.* Between 90–110° an oil passed over, but it was only slightly soluble in water, and certainly did not contain more than a trace of aldol.

These results led us to examine the behavior of aldol towards potassium formate, under like conditions. This compound was completely decomposed into the same products obtained from ethyl aldehyde. It is evident that the conditions of the experiment precluded the existence of aldol, even if it had been formed in the reaction. In the second experiment a dilute solution of potassium formate was used. Two grams of the salt were dissolved in 40 grams of distilled water, and the solution mixed with an equal volume of ethyl aldehyde. This mixture was heated in a sealed tube for six hours at 100°, and gave after heating a homogeneous liquid, smelling slightly of crotonic aldehyde. The undecomposed ethyl aldehyde was expelled by gentle heating, the liquid extracted with ether, and the residue remaining after evaporation of the ether distilled *in vacuo.* Between 90–110° a considerable quantity of a liquid passed over, which an examination showed to be aldol. Several experiments were made in order to ascertain the minimum concentration of aqueous potassium formate which would form aldol. A solution of 1 gram of salt in 40 grams of water and an equal volume of aldehyde gave, after heating 48 hours, a considerable amount of aldol; while a solution containing but 0.5 gram of salt and the other compounds as above, did not yield aldol, even after heating several days.

It may be inferred with considerable certainty that the formation of crotonic aldehyde by the action of potassium formate is preceded by the formation of β-oxybutyric aldehyde. The property of carbon-polymerising ethyl aldehyde to aldol is not confined to potassium formate. It was shown by every potassium salt we examined whose aqueous solution possesses an alkaline reaction, and it only needs the confirmation of experiment to give certainty to the generalisation that all such potassium compounds have this property. A solution of 15 parts of dipotassium phosphate in 30 parts of water, and ethyl aldehyde added until the salt began to separate, contained aldol after heating. A small quantity of an oil, containing crotonic aldehyde, separated from the liquid, probably due to the action of the salt on aldol.

A tube with potassium acetate, prepared like the above, also gave aldol. In this experiment a much larger amount of oil had separated from the solution.

The same result was obtained by using an aqueous solution of potassium carbonate. Very interesting is the action of the dry salt on aldehyde. Bruylants,[1] who had already made this experiment, found that the aldehyde was completely converted into resinous products. The action is indeed very violent, and nothing but resinous products are obtained, unless care be taken to cool the aldehyde and carbonate before bringing them together. With this precaution, however, the reaction proceeds slowly, and after several hours the mixture may be allowed to stand at the ordinary temperature. After standing two days the liquid had assumed the consistency of aldol, and the carbonate was dissolved in the liquid. The slightly yellow liquid was dissolved in water, the solution extracted with ether, and the extract treated in the usual way for the preparation of aldol. The yield of this substance was so considerable that we can recommend the method for its preparation.

The neutral potassium salts examined in respect to their behavior towards ethyl aldehyde, were the sulphate, nitrate and chloride. Mixtures of two parts of aldehyde and one of water were saturated with these salts, and heated in closed tubes at 100°. In no case, even after prolonged heating, was a change noticed in the contents of the tubes.

The action of potassium salts whose aqueous solutions show an alkaline reaction may be owing to the presence of a small amount of free alkali in the solution, as it is not improbable that the alkaline reaction is due to a slight decomposition of such salts into free alkali and an acid salt. Lieben had already made an experiment on the action of potassium hydrate on aldehyde, in the hope of obtaining crotonic aldehyde. A heavy red liquid, insoluble in water, was obtained, which was considered as an intermediary product between crotonic aldehyde and aldehyde-resin. We can confirm this result, but the oil is only formed by long heating from the first product of the reaction. If a very dilute solution of caustic potash is mixed with an equal volume of aldehyde, and the mixture heated for two hours at 90°, but little of this oil separated from the liquid. Extracted with ether and examined for aldol, the presence of this compound was shown. Aldol, when heated with dilute aqueous caustic potash, is gradually converted into the heavy oil. There is, however, no proof that the salts themselves do not possess the property of forming aldol; indeed, in one instance, its formation by the action of dry potassium carbonate on anhydrous aldehyde, this has been shown to be the case.

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[1] Berichte der deutschen chemischen Gesellschaft, 8, 415.

Action of Sodium Salts on Ethyl Aldehyde.

Lieben in his experiments on the action of sodium acetate used a concentrated solution of that salt, and obtained crotonic aldehyde. The experiment was repeated, with the difference that the tube was heated only to 80° for ten hours. After heating the liquid was separated into two layers. The supernatant liquid, distilled *in vacuo*, gave crotonic aldehyde, and an oily, higher boiling liquid, which was insoluble in water. This oil may have been formed by the action of the salt on crotonic aldehyde, since it was found that the same, or a very similar product, can be obtained by heating crotonic aldehyde with aqueous sodium acetate. The lower layer was extracted with ether, the ether evaporated, and the oily residue extracted with a small amount of water. The greater part of the oil did not dissolve in it; on distillation *in vacuo*, crotonic aldehyde was obtained. The soluble portion, on evaporation *in vacuo*, left an extremely small amount of a thick liquid, which but partly dissolved on second treatment with water. It is possible that this liquid contained a minimum amount of aldol, but the quantity of the liquid obtained was too small to permit its isolation. The reaction was then examined, using dilute solutions of sodium acetate. Under these conditions a somewhat greater quantity of the soluble thick liquid was obtained, but not enough to purify it by distillation. We believe that a small amount of aldol is formed in the reaction; it was very evident, however, that in all of our experiments crotonic aldehyde, and compounds decomposing into it on distillation, are the main products of the reaction.

Potassium formate acts readily on aldehyde, forming aldol; in striking contrast appears the following experiment with sodium formate. A mixture of equal volumes of aldehyde and a saturated solution of sodium formate was heated for several days at 100°. The salt is but slightly soluble in concentrated aqueous aldehyde. On heating at 100° more dissolved and crystallised out from the solution on cooling. The aldehyde was found to remain unchanged.[1] A tube with disodium phosphate was prepared by mixing equal volumes of a saturated aqueous solution of the salt and ethyl aldehyde, and then adding sufficient water to dissolve the salt which had separated. After heating at 100° the supernatant oil of the liquid was found to distill between 80° and 210°, and yielded mainly crotonic aldehyde. The aqueous solution gave the same results as the experiment with sodium acetate.

Very noteworthy is the difference between the behavior of sodium and potassium carbonates. Dry sodium carbonate is, at ordinary temperature, without action on anhydrous aldehyde; even if allowed to stand in contact with it for several months.

Like the neutral potassium salts, solutions of the corresponding sodium salts were found to be without action on ethyl aldehyde.

Finally a very dilute solution of sodium hydrate was heated with aldehyde. The results were about the same as those obtained with potassium hydrate. A sufficient quantity of aldol was obtained to prove its formation beyond a doubt, but the amount formed under the same conditions was much less than with the potassium compound.

The following are the principal results of the investigation:

1. The primary product of the action of zinc chloride on ethyl aldehyde is β-oxybutyric aldehyde.

2. Neutral sodium and potassium salts have no action on ethyl aldehyde.

3. Alkaline potassium salts, sodium and potassium hydrates act like zinc chloride. The presence of water is not always necessary, as dry potassium carbonate acts in the same manner.

4. Alkaline sodium salts, under the same conditions as potassium salts, form principally crotonic aldehyde, oily substances, and probably a small amount of β-oxybutyric aldehyde. Dry sodium carbonate has no action on aldehyde.

5. β-oxybutyric aldehyde heated with moderately concentrated solutions of alkaline salts or zinc chloride, is converted partly in crotonic aldehyde, and partly in higher boiling oils, that decompose into crotonic aldehyde on distillation. Crotonic aldehyde itself undergoes a change to higher boiling products.

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[1] Experiments with dilute solutions of this salt were also made. Unfortunately the results were not written down in our notebook. We believe that a small amount of oily products, giving crotonic aldehyde on distillation, were obtained, but no aldol, at least not in appreciable quantity.

It would be premature to discuss whether, in the action of alkaline sodium salts, the formation of crotonic aldehyde is preceded by that of β-oxybutyric aldehyde. The experiments with sodium and potassium formates, carbonates and phosphates show, beyond a doubt, that potassium salts possess in a much greater degree than sodium salts the property of carbon-polymerising ethyl aldehyde. This is a clue to the function of potassium salts in the vegetable world that should not be lost sight of. The retention of potassium salts by the soil, their absorption by plants as essential constituents for life, and the property of these salts of converting aldehydes into oxyaldehydes of higher series, are evidently intimately related; especially as recent researches have made it probable that the first product in the formation of the carbohydrates is the aldehyde of the methyl group.[1]

COLLEGE HILL, MASS., *June 20th*, 1883.

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[1] We made a large number of experiments on the action of potassium salts on methyl aldehyde (see Bulletin de la Société chimique (1879), **31**, 434; this Journal, **1**, 418). The salts used were potassium carbonate, formate and phosphate. The proportion was about one part of salt to ten parts of aldehyde in aqueous solution, and the experiments were made in closed tubes heated at 100°. The product of the reaction contains a dark colored syrup, which was purified by partial precipitation with basic lead acetate, filtration from the dark precipitate, and repeating until a white precipitate was obtained, which was suspended in water and treated with hydrogen sulphide. The filtrate was evaporated to dryness and the residue extracted with absolute methyl alcohol, filtered and again evaporated. The syrup, which had a slightly bitter taste, reduced Fehling's solution, apparently however not so strongly as dextrose does. It gradually hardened, but no sign of crystallisation was observed, even on standing several months. Heated with acetic anhydride and sodium acetate, a syrup, insoluble in water, was formed, but a crystalline product was not formed, as might be expected if the syrup contained dextrose. The analysis of the lead compound showed that the constitution of the syrup differed somewhat according to the conditions of its preparation. The results were, 67.3, 67.6, 68.1, 67.9 per cent. of PbO. According to Pelletier and Stein, the corresponding lead derivative of dextrose contains 66.27 per cent. of PbO. The proximate analysis of the syrup, dried at 100°, gave the following numbers:

		Found		Theory for	
				$C_6H_{10}O_5$	$C_6H_{12}O_6$
C	42.9	43.4	43.7	44.4	40.0
H	6.3	6.2	6.6	6.17	6.6

The analyses were made with products of different preparations. It is probable that the syrup obtained by the action of alkaline potassium salts is the same as that obtained by Butlerow by the action of alkalies or barium hydrate; a reaction which has lately been re-examined by Tollens (Berichte der deutschen chemischen Gesellschaft, **16**, 919).

LABORATORY NOTES.—II.[1]

By Arthur Michael.

V.—ON THE ACTION OF SODIUM ETHYL OXIDE ON BROMETHYLIDENEBROMIDE.

According to Tawildarow[2] sodium ethyl oxide acts on bromethylidenebromide, forming a mixture of two dibromethylenes; the bromide boiling at 91°, and a second compound boiling at 157°. A third isomeride, boiling at 109°, has been obtained by Sabenejeff;[3] either by direct addition of bromine to acetylene, or by reduction of acetylene tetrabromide. The existence of three dibromethylenes is of great theoretical importance, since it necessitates the assumption of a so-called dyad carbon atom in one of the compounds. The bromethylidenebromide used by Tawildarow was isolated from the products of the action of bromine on ethylbromide; and, as the perfect separation of the products of that reaction is somewhat difficult, it was thought of sufficient interest to repeat his experiment, using a pure product obtained by the addition of bromine to bromethylene. It may be mentioned that Tawildarow supposed the product boiling at 157° to be identical with acetylene dibromide, and that the later investigation of Sabenejeff, and also that of Anschuetz,[4] show that this is not the case.

The experiment was repeated under exactly the conditions stated by Tawildarow. The formation of bromacetylene was noticed. The greater part of the product of the reaction passed over under 95°, and gave on redistillation α-dibromethylene, boiling at 86–88°. Above 95° the thermometer rose rapidly to 180–190°, at which temperature undecomposed bromethylidenebromide passed over. The products of the reaction of equal molecules of sodium ethyl oxide and bromethylidenebromide (from bromethylene) are, therefore, bromacetylene, α-dibromethylene and unchanged bromethylidenebromide. The results of the analyses and vapor density given by Tawildarow for the dibromethylene boiling at 157°, agree fairly with the numbers required by theory; but before so important a fact as the existence of a third dibromethylene can be accepted, more decisive proof of the homogeneity and nature of the product is necessary; especially in view of the result obtained from the pure bromethylidenebromide used in the above-described experiment.

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[1] This Journal, **1**, 413.

[2] Annalen der Chemie, **176**, 22.

[3] *Ibid.* **178**, 116; Berichte der deutschen chemischen Gesellschaft, **9**, 1441.

[4] Berichte der deutschen chemischen Gesellschaft, **12**, 2073.

It may not be unprofitable to review the recent discussions on the constitution of the dibromethylene boiling at 88°. Demole, in his first paper, when he showed that this compound absorbs free oxygen passing over into bromacetylbromide, assumed that the dibrom compound was identical with acetylene dibromide, and attempted to explain the formation of bromacetylbromide by a transposition of an hydrogen atom and direct addition of oxygen: $\begin{matrix}\mathrm{CHBr}\\ \mathrm{CHBr}\end{matrix}+\mathrm{O}=\begin{matrix}\mathrm{CH_2Br}\\ \mathrm{COBr}\end{matrix}$. Fittig called attention to the extreme improbability of such a reaction, and proposed, as best explaining its properties, the formula $\mathrm{CH_2Br{-}CBr}$. The next contribution was made by Anschuetz,[1] who, by confirming Sabenejeff's experiments on acetylene dibromide, showed that chemist's compound is identical with the dibromide in question. Demole[2] had, in the meantime, arrived at the same conclusion in a different manner. He examined the action of aluminium chloride on a mixture of dibromethylene (88°) and benzene, and obtained unsymmetrical diphenylethylene. Although Demole accepted Fittig's formula as the simplest explanation of the behavior of dibromethylene towards oxygen, he considered the formation of unsymmetrical diphenylethlylene as a conclusive proof of an unsymmetrical distribution of the bromine in α-dibromethylene. A compound of the formula $\mathrm{CH_2Br{-}CBr}$ should have given $\mathrm{C_6H_5{-}CH_2{-}C{-}C_6H_5}$; the reaction which took place is represented, according to Demole, as follows:

$$\mathrm{CBr_2{-}CH_2+2C_6H_6=C(C_6H_5)_2{-}CH_2+2HBr.}$$

This experiment seems to have been very generally accepted as proving the constitution of α-dibromethylene. In reality the experiment gives no decisive proof in regard to the constitution of that compound, as it depends entirely on the interpretation which has been given to the reaction. It is a well-known property of the halogen derivatives of unsaturated hydrocarbons that the halogen atoms are either not replaceable, or only with difficulty, by other groups. In this respect there is but little difference between the aromatic and paraffin compounds; the halogen derivatives of benzene act like the halogen derivatives of an alkylene, or, more strictly, an alkylacetylene, in which the halogen is connected with an unsaturated carbon atom. The proof that these unsaturated halogen hydrocarbons act in the Friedel reaction like the saturated compounds is still to be given. It is improbable, in view of the difficulty with which this class of compounds enter into double decompositions. The reaction examined by Demole is susceptible of quite a different interpretation. Shortly before, Balsohn[1] had shown that ethylene passed into the benzene-aluminium chloride mixture is absorbed with the formation of ethylbenzene. Here we have a reaction which is analogous to Demole's. If ethylene unites to form ethylbenzene, dibromethylene will unite, probably with much greater ease, to form dibromethylbenzene. In this saturated compound the conditions are given for the replacement of bromine by phenyl by means of Friedel's reaction. From $CBr_2—CH_2$ the compounds $CBr_2C_6H_5—CH_3$ or $CBr_2H—CH_2C_6H_5$, from $CH_2Br—CBr$, the compound $CH_2Br—CBrHC_6H_5$ may be formed; and it is evident that from the first and third of these compounds, by replacing a bromine by phenyl and splitting off of bromhydric acid, unsymmetrical diphenylethylene may be obtained:

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[1] Berichte der deutschen chemischen Gesellschaft, **12**, 2073.

[2] *Ibid.* **12**, 2245.

$$CH_2Br — CBr + C_6H_6 = CHBr_2 — CHBrC_6H_6$$
$$CH_2Br — CHBrC_6H_5 + C_6H_6 = CH_2Br — CH(C_6H_5)_2$$
$$CH_2Br — CH(C_6H_5)_2 = CH_2 — C(C_6H_5)_2 + HBr.$$

Demole[2] published in the following year a new series of experiments on the action of oxygen on α-dibromethylene. In this paper the previous explanation is given up, because an experiment showed that oxygen and bromhydric acid passed into bromacetylene do not yield bromacetylbromide. He now considered the reaction as due to the displacement of bromine by oxygen, and addition of bromine to the hypothetical compound thus formed. Demole's method of proof is here exactly as decisive as in his previous papers. Certain well-known reactions are given a dogmatic interpretation, and it is applied to the reaction in question. When bromine separates from a concentrated solution of bromhydric acid exposed to the action of oxygen, it is, according to

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[1] Bulletin de la Société chimique, **31**, 540.

[2] *Ibid.* **34**, 201.

Demole, due to the displacement of bromine by oxygen. How will he prove that it is not due to the oxidation of bromhydric acid to hypobromous acid, which, as is well known, is decomposed by bromhydric acid into bromine and water? Again, a large number of bromides when exposed to the air attract water, and are converted into acids. When phosphorus tribromide is converted by water into phosphorous acid, according to Demole, the water is first decomposed into hydrogen and oxygen, the latter element then displaces the bromine, which unites with the hydrogen, and finally the acid anhydride takes up water to form phosphorous acid. The usual interpretation is, of course, a simple double decomposition between the water of the air and the tribromide. As further proof, an exceedingly interesting experiment on the action of oxygen on boiling phosphorus tribromide is given. The products formed are phosphorus pentabromide and oxybromide. The conclusion drawn from the experiment is, that oxygen displaces bromine to form POBr, which unites with bromine to form $POBr_3$, and with PBr_3 to give PBr_5. Unexplained is how two atoms of bromine do the work of four; or else the liquid contained POBr, a point still to be proven. It is at present impossible to give any decisive proof regarding the formation of the pentabromide. Homogeneous phosphorus trichloride is perhaps entirely unknown. As Casselmann[1] has shown the distilled compound deposits phosphorus, it consists, not unlikely, of a large proportion of trichloride with phosphorus and pentachloride. A decisive proof that the formation of oxychloride by the action of oxygen on trichloride is due to the direct addition of oxygen to the trichloride has yet to be given. Or, it is possible that, under the above conditions, $POBr_3$ may act on PBr_3, forming oxide and pentabromide. Finally, dried air was passed for ten hours through α-dibromethylene. The gases passed out through a series of well-cooled tubes, and then into a flask containing bromine. This flask was found to contain tetrabromethene, and the first vessel bromacetylbromide, bromacetic acid and a polymeride of $C_2H_2Br_2$. The explanation: oxygen breaks, in a peculiar manner (*façon speciale*), the "double carbon-link" forming the compound $—CBr_2—CH_2—$. This product is extremely volatile — so much that it passed through a tube surrounded by a mixture of ice and salt, and was absorbed in the bromine flask, forming $CBr_3—CH_2Br$. The compound also undergoes, especially at a high temperature, a decomposition represented as follows: $-CH_2-CBr_2- + O = -CH_2-C=O + Br_2$; $-CH_2-CO- + Br_2 = CH_2Br-COBr$. The climax of the double and triple linkage theory has here been reached. This theory supposes that there are no less than three different kinds of linkage; or, rather, carbon may be linked to carbon in three different ways. In the first kind the carbon atoms, as in saturated hydrocarbons, are not "ruptured" by the action of halogens; the second variety of linkage is shown in unsaturated hydrocarbons, where a "rupture" occurs until the compound becomes saturated; and, finally, the existence of a third variety is supposed, where, even in saturated compounds, a "rupture" takes place, but on reduction with nascent hydrogen it is healed. And now Demole supposes that a characteristic property of compounds with ruptured carbon-linkage is extreme volatility.

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[1] Annalen der Chemie, **83**, 267.

It may be well, before proceeding further in this maze of hypotheses regarding double and triple linkage, to inquire for its credentials. .How do we know that double or triple linkage occurs in unsaturated organic compounds? What facts necessitate this hypothesis? But two plausible reasons have been brought forward. The attempts that have been made to obtain methylene and ethylidene have not succeeded, in each case ethylene gas was obtained; and that methyl is not known in a free state. The experiments with methyleneiodide prove nothing in regard to a possible existence of methylene. The first product in the action of copper, reasoning from analogy with methyliodide, is ethyleneiodide, which, as is well known, on heating with metals goes over into ethylene. The same applies to the action of sodium at a high temperature on ethylidenechloride. There is no necessity for supposing the previous formation of ethylidene; the chloride heated to a high temperature gives off chlorhydric acid,[1] and this will naturally occur much more readily in the presence of a substance like sodium, which has a strong affinity for the acid. Given chlorhydric acid, sodium and chlorethylene, and we have all the conditions requisite for the formation of ethylene. Equally cogent is the non-existence of methyl. All that can be said on the subject is, that it is a property of this radical, under the conditions of the experiments, to pass over into a saturated hydrocarbon. But if compounds like methylene and ethylidene are

[1] Kraemer, Berichte der deutschen chemischen Gesellschaft, **12**, 204.

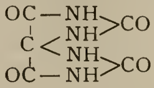
not known, it is only necessary that part or all of the hydrogen of these hydrocarbons should be replaced by negative elements or groups to give stable compounds. The existence of CO, of $CH_3 — N — C$, of $HOOC — CH_2 — C — COOH$, and probably of $CH_2Br — CBr$, shows this beyond a doubt. A general property of this class of substances is the marked affinity of the unsaturated carbon for oxygen. CH_3NC and HgO give CH_3NCO, and Demole has shown the still more pronounced affinity of $CH_2Br — CBr$. I have used Demole's researches as an example of the deteriorating influence which the double and triple linkage hypothesis is exerting in theoretical chemistry. It would be an easy matter to name a long list of similar theoretical contributions.

The only hypothesis that offers any explanation for the properties of unsaturated organic compounds is that which supposes the maximum combining capacity of certain of the constituent elements not to be reached. It is obvious, that this is best ascertained by the behavior of the compound toward halogens; but in all cases the constitution of the products must be fully understood before any conclusion should be drawn. The behavior of saturated hydrocarbon towards halogens shows clearly that the affinity which is called a carbon link is not broken in the action of halogens on hydrocarbons. Therefore, when it is found that a compound like ethylene takes up readily two bromine atoms to form symmetrical dibromethene, the only conclusion that can be logically drawn is, that it contained two carbon atoms whose maximum combining capacity is reached by uniting with a bromine atom. Any other inference is without a scientific basis: as that one-fourth of the combining capacity of the carbon was unsaturated, or that the combinations were doubly linked; superfluous and unproven in the first, contradictory to all that is known concerning the union of carbon to carbon in the second.

To return to Demole's last research. It may be well to call attention that a definite proof of oxygen being necessary for the formation of tetrabromethene in the bromine tube has yet to be given. If it were found that when nitrogen is passed through α-dibromethylene, kept at the temperature which the chemical action of oxygen causes the liquid to take, bromacetylene is not formed, or that the latter compound is not formed by keeping α-dibromethylene for a long time at a moderate heat, then a connection may be assumed with some degree of certainty.

VI.—A NEW SYNTHESIS OF ALLANTOÏN AND SOME SUGGESTIONS ON THE CONSTITUTION OF URIC ACID.

For reasons, which will be stated below, several attempts were made to obtain mesoxalyldiureide synthetically:



$$\begin{array}{l}\mathrm{OC-NH}\\ \;|\qquad\quad\;\;>\mathrm{CO}\\ \mathrm{C<NH}\\ \quad\;\;\mathrm{NH}\\ \;|\qquad\quad\;\;>\mathrm{CO}\\ \mathrm{OC-NH}\end{array}$$

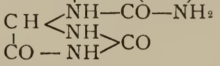
A mixture of equal weights of mesoxalic acid and carbamide was heated in an oil-bath at 110°. An homogeneous liquid was formed, and carbon dioxide given off. After heating several hours the product of the reaction was extracted with boiling water. From the extract prismatic crystals separated on cooling. These were allantoïn, as was shown by an analysis and examination of their properties.

0.3555 gram gave 0.3976 gram CO_2 and 0.1248 gram H_2O.

	Theory for $C_4H_6N_4O_3$.	Found.
C	30.37	30.51
H	3.77	3.90

The formation of allantoïn from mesoxalic acid and urea is represented as follows:

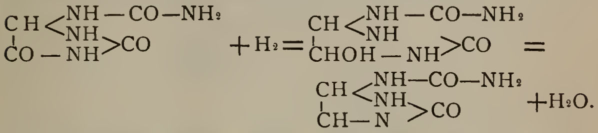
$$COOH - C(OH)_2 - COOH + 2\,CO(NH_2)_2 =$$



$$\begin{array}{l}\mathrm{CH<NH-CO-NH_2}\\ \;|\qquad\mathrm{NH}\\ \;|\qquad\qquad\;>\mathrm{CO}\\ \mathrm{CO-NH}\end{array} + CO_2 + 3H_2O.$$

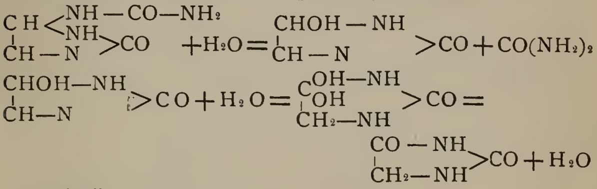
Mesoxalic acid may be heated for some hours at 110° without undergoing a noticeable decomposition, but when heated in presence of other substances it has a great tendency to split off carbon dioxide. An experiment with the same mixture, and using phosphorus trichloride as a dehydrating agent, was next made at a lower temperature (80°). The evolution of carbon dioxide was again observed. From the products of the reaction an amorphous yellow substance was isolated, which did not yield alloxan when heated with nitric acid, and was not further examined. A similar result was obtained by the action of phosphorus trichloride on a mixture of alloxanic acid and carbamide. As oxalylureide is said to be formed by the action of oxalic ether on carbamide, an analogous experiment was made with mesoxalic ether, but no action was observed, either on boiling the mixture in an open vessel, or by heating it in a closed tube.

The empirical formula of mesoxalyldiureide, $C_5H_4N_4O_4$, differs from that of uric acid by an additional atom of oxygen. The reduction of uric acid to xanthine needs confirmation,[1] but there can be no doubt that from allantoïn a compound containing one atom less of oxygen has been obtained by reduction.[2] The formation of glycoluril may be represented as follows:



$$\left.\begin{array}{l}\mathrm{CH}<^{\mathrm{NH-CO-NH_2}}_{\mathrm{NH}}\\ \;|\\ \mathrm{CO-NH}\end{array}\right>\mathrm{CO} + \mathrm{H_2} = \left.\begin{array}{l}\mathrm{CH}<^{\mathrm{NH-CO-NH_2}}_{\mathrm{NH}}\\ \;|\\ \mathrm{CHOH-NH}\end{array}\right>\mathrm{CO} = \left.\begin{array}{l}\mathrm{CH}<^{\mathrm{NH-CO-NH_2}}_{\mathrm{NH}}\\ \;|\\ \mathrm{CH-N}\end{array}\right>\mathrm{CO} + \mathrm{H_2O}.$$

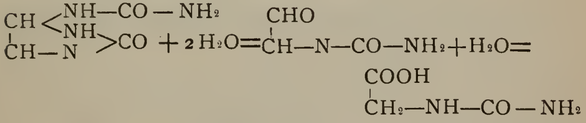
The decomposition of this compound by acids:



$$\left.\begin{array}{l}\mathrm{CH}<^{\mathrm{NH-CO-NH_2}}_{\mathrm{NH}}\\ \;|\\ \mathrm{CH-N}\end{array}\right>\mathrm{CO} + \mathrm{H_2O} = \left.\begin{array}{l}\mathrm{CHOH-NH}\\ \;|\\ \mathrm{CH-N}\end{array}\right>\mathrm{CO} + \mathrm{CO(NH_2)_2}$$

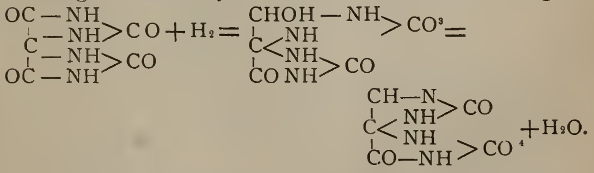
$$\left.\begin{array}{l}\mathrm{CHOH-NH}\\ \;|\\ \mathrm{CH-N}\end{array}\right>\mathrm{CO} + \mathrm{H_2O} = \left.\begin{array}{l}\mathrm{C}^{\mathrm{OH-NH}}_{\mathrm{OH}}\\ \;|\\ \mathrm{CH_2-NH}\end{array}\right>\mathrm{CO} = \left.\begin{array}{l}\mathrm{CO-NH}\\ \;|\\ \mathrm{CH_2-NH}\end{array}\right>\mathrm{CO} + \mathrm{H_2O}$$

By alkalies:



$$\left.\begin{array}{l}\mathrm{CH}<^{\mathrm{NH-CO-NH_2}}_{\mathrm{NH}}\\ \;|\\ \mathrm{CH-N}\end{array}\right>\mathrm{CO} + 2\,\mathrm{H_2O} = \begin{array}{l}\mathrm{CHO}\\ \;|\\ \mathrm{CH-N-CO-NH_2}\end{array} + \mathrm{H_2O} = \begin{array}{l}\mathrm{COOH}\\ \;|\\ \mathrm{CH_2-NH-CO-NH_2}\end{array}$$

Starting from mesoxalyldirureide a similar reaction would give:



$$\begin{array}{l}\left.\begin{array}{l}\mathrm{OC-NH}\\ \;|\;\;\mathrm{-NH}\end{array}\right>\mathrm{CO}\\ \mathrm{C}\\ \left.\begin{array}{l}\;|\;\;\mathrm{-NH}\\ \mathrm{OC-NH}\end{array}\right>\mathrm{CO}\end{array} + \mathrm{H_2} = \begin{array}{l}\mathrm{CHOH-NH}\!>\mathrm{CO}^{[3]}\\ \;|\;\;\mathrm{NH}\\ \mathrm{C}<\\ \;|\;\;\mathrm{NH}\!>\mathrm{CO}\\ \mathrm{CO\,NH}\end{array} = \begin{array}{l}\mathrm{CH-N}\!>\mathrm{CO}\\ \;|\;\;\mathrm{NH}\\ \mathrm{C}<\\ \;|\;\;\mathrm{NH}\!>\mathrm{CO}\\ \mathrm{CO-NH}\end{array}{}^{[4]} + \mathrm{H_2O}.$$

---

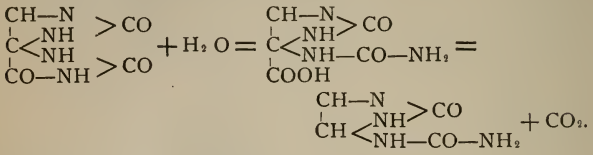
[1] Annalen der Chemie, **131**, 121.

[2] *Ibid.* **134**, 219.

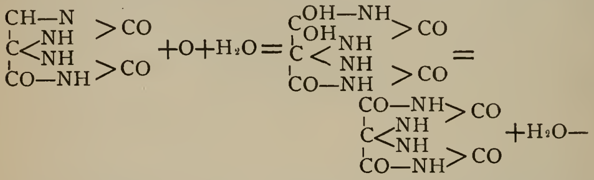
[3] The formation of $\mathrm{CO}<^{\mathrm{NCH_3-CHOH}}_{\mathrm{NCH_3-CO}}$ from $\mathrm{CO}<^{\mathrm{NCH_3-CO}}_{\mathrm{NCH_3-CO}}$ by reduction. (Andreasch, Monatshefte für Chemie, **3**, 432.)

[4] The behavior of acetylacetic ether, of malonic ether, and more especially, according to the experiments of Conrad and Guthzeit (Berichte der deutschen chemischen Gesellschaft, **14**, 1643; **15**, 2844), of malonylureide towards bases, show that Hill and Mabery's investigation on dimethyluric acid cannot be accepted as conclusively proving that uric acid contains four NH groups.

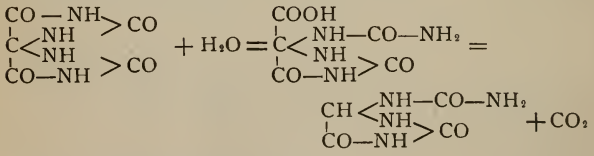
The first product of the decomposition of uric acid by acids should be glycoluril, which, however, would be further decomposed, at the high temperature used in this reaction, into amido-acetic acid, carbon dioxide and ammonia:



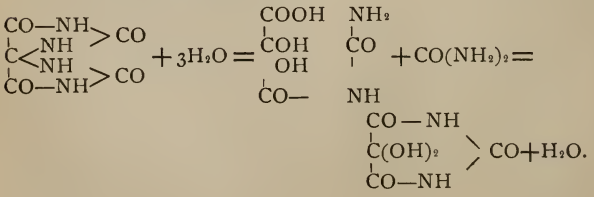
In the presence of oxidising agents an atom of oxygen and water are added, forming the unstable mesoxalyldiureide, which is further decomposed according to the conditions of the experiment:



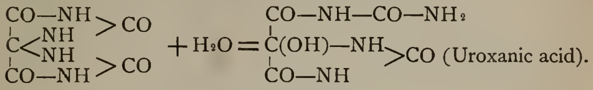
If the oxidation is effected in an alkaline solution this compound decomposes into allantoïn.



In an acid solution (nitric acid),

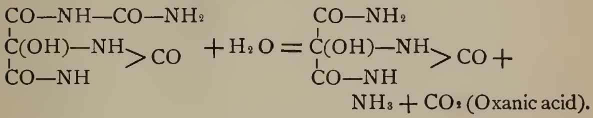


This reaction appears anomalous, but an analogy is found in the conversion of alloxan into oxalylurea by the action of nitric acid. When uric acid in alkaline solution stands exposed in the air for a long time, uroxanic and oxanic acids are formed:



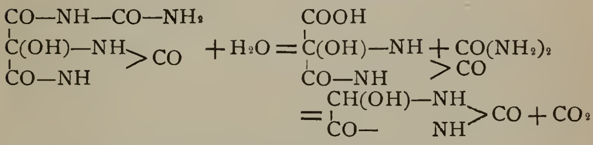
$$\begin{array}{l}CO-NH\\ C<^{NH}_{NH}\\ CO-NH\end{array}\begin{array}{l}>CO\\ \\ >CO\end{array} + H_2O = \begin{array}{l}CO-NH-CO-NH_2\\ C(OH)-NH\\ CO-NH\end{array}\!\!>CO \text{ (Uroxanic acid).}$$

The further action of alkali on this acid:



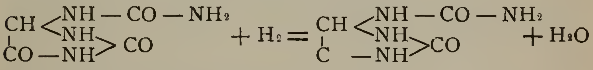
$$\begin{array}{l}CO-NH-CO-NH_2\\ C(OH)-NH\\ CO-NH\end{array}\!\!>CO + H_2O = \begin{array}{l}CO-NH_2\\ C(OH)-NH\\ CO-NH\end{array}\!\!>CO + NH_3 + CO_2 \text{ (Oxanic acid).}$$

Both these acids go over into allanturic acid:



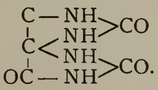
$$\begin{array}{l}CO-NH-CO-NH_2\\ C(OH)-NH\\ CO-NH\end{array}\!\!>CO + H_2O = \begin{array}{l}COOH\\ C(OH)-NH\\ CO-NH\end{array}\!\!>CO + CO(NH_2)_2 = \begin{array}{l}CH(OH)-NH\\ CO-\quad NH\end{array}\!\!>CO + CO_2$$

A second possible formula for glycoluril is:



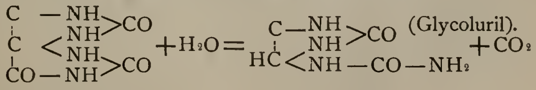
$$\begin{array}{l}CH<^{NH-CO-NH_2}_{NH}\\ CO-NH\end{array}\!\!>CO + H_2 = \begin{array}{l}CH<^{NH-CO-NH_2}_{NH}\\ C\quad -NH\end{array}\!\!>CO + H_2O$$

The corresponding formula for uric acid is:

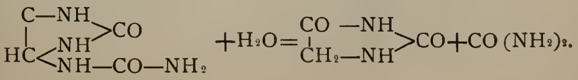


$$\begin{array}{l}C-NH\\ C<^{NH}_{NH}\\ OC-NH\end{array}\begin{array}{l}>CO\\ \\ >CO.\end{array}$$

This formula, probably, is more in accordance with the properties of uric acid than the first. It expresses the marked affinity of uric acid for oxygen much more clearly, and equally well the formation of amidoacetic acid by heating with acids:



$$\begin{array}{l}C\quad -NH\\ C\;<^{NH}_{NH}\\ CO-NH\end{array}\begin{array}{l}>CO\\ \\ >CO\end{array} + H_2O = \begin{array}{l}C-NH\\ \quad\;\; NH\\ HC<NH-CO-NH_2\end{array}\!\!>CO \text{ (Glycoluril).} + CO_2$$



$$\begin{array}{l}C-NH\\ \quad\;\; NH\\ HC<NH-CO-NH_2\end{array}\!\!>CO + H_2O = \begin{array}{l}CO\;-NH\\ CH_2-NH\end{array}\!\!>CO + CO(NH_2)_2.$$

Perhaps either of these formulæ of uric acid is more strictly based on analogy with the properties and decompositions of the derivatives of uric acid than any as yet proposed; but they would hardly be worthy of publication did they not indicate a possible way to a synthesis of uric acid, which would not fail to throw a strong light on its constitution. Among the numerous experiments that still suggest themselves for the synthesis of mesoxalyldiureide, the action of dibrommalonic acid on the silver derivative of carbamide, or the action of the chloride of that acid on carbamide, may be mentioned.

VII.—ON A CONVENIENT METHOD FOR PREPARING BROMACETIC ACID.

The preparation of bromacetic acid in large quantity by heating acetic acid with bromine in closed tubes is exceedingly tedious, so that the following method, which I and friends to whom it has been communicated have had occasion to use during the past five years, will be found very advantageous. It is based on the decomposition of $(C_2H_4O_2Br_2)_4HBr$ at 100° under ordinary pressure into bromacetic acid and bromhydric acid. Hell and Muhlhäuser,[1] who examined this remarkable compound, attempted to make use of its properties for the preparation of bromacetic acid; but, as they heated it in closed tubes, found the method impracticable on account of the tubes exploding.

A mixture of acetic acid and bromine, in equivalent proportions, and a small amount of carbon disulphide is heated at 100° in a flask with a return cooler until bromhydric acid ceases to be given off. As a small amount of the bromine escapes through the cooler, somewhat more than the theoretical amount may be taken with advantage. It is absolutely necessary, if good results are to be obtained, to use all the reagents in a perfectly anhydrous condition; indeed, on acetic acid containing more than several per cent. of water no action takes place. From the product of the reaction about 90 per cent. of the theoretical amount of bromacetic acid may be obtained by fractional distillation.

Noteworthy is the observation that no dibromacetic acid is formed, even when bromine is used in large excess. Also, that this method cannot be used for the preparation of brompropionic nor brombutyric acids. It is possible, however, that the acids used in these experiments contained a small quantity of water, which, as is the case with acetic acid, may have prevented the reaction.

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 241.

VIII.—ON SEVERAL CASES OF INTERMOLECULAR REARRANGEMENT.

It is at present pretty generally understood that what is called intermolecular rearrangement often represents the final step in a series of changes. The consideration of intermolecular rearrangement in this light has shown, in a number of instances, that the intermediate reactions explain the final result.[1]

By the action of zinc-methyl on ethylene-iodohydrine, Butlerow and Ossokin[2] obtained secondary propylalcohol, instead of the primary compound, as was expected. It is possible that this result is due to the previous formation of ethylaldehyde. Wislicenus[3] has shown that sodium acts on monochloracetal to form $CH_2 - CH - O - C_2H_5$, and that this compound, on decomposition by dilute sulphuric acid, gives ethylaldehyde and alcohol. According to Butlerow and Ossokin, the first product of the action of zinc-methyl is $CH_2I - CH_2 - OZnCH_3$, and this compound, heated to a high temperature with an excess of zinc-methyl, gives $CH_3 - CH{<}^{OZnCH_3}_{CH_3.}$ The following equations may represent the various stages of this reaction:

$$
\begin{aligned}
&CH_2I - CH_2 - OZnCH_3 = CH_2 - CH - OZnCH_3 + HI \\
&CH_2 - CH - OZnCH_3 + HI = CH_2 - CHOH + ZnI(CH_3) \\
&CH_2 - CHOH = CH_3 - CHO \\
&CH_3 - CHO + 2ZN(CH_3)_2 = CH_3 - CH{<}^{OZnCH_3}_{CH_3}
\end{aligned}
$$

Anschuetz[4] has observed that a trace of iodine heated with ethyl malate suffices to convert the compound into ethyl fumarate. The formation of fumaric ether is probably preceded by that of a trace of iodohydric acid, which unites with an equal number of molecules of ethyl malate, forming ethyl iodosuccinate. The interesting experiments of Fittig[1] on the behavior of fumaric and maleic acids towards bromhydric acid, have shown that maleic acid combines much more readily with it than fumaric acid does; in other words, it has a stronger affinity for it. Now, bromsuccinic acid decomposes when heated above its melting-point into fumaric and bromhydric acids, and this decomposition can but take place more easily when a substance like maleic acid, having a strong affinity for bromhydric acid, is present. The conversion of maleic ether into fumaric ether may therefore be considered as the final result of a series of additions of iodohydric acid to ethyl malate and decompositions of the ethyl iodosuccinate into fumaric ether and iodohydric acid.

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[1] As is the case in the conversion of dimethylaniline chlorhydrate into the salt of amidodimethylbenzene. (This Journal, **1**, 420; Berichte der deutschen chemischen Gesellschaft, **13**, 2108.) It is much to be hoped that the use of the phrase "atomic migration," which is a misnomer and unscientific, will be discontinued.

[2] Annalen der Chemie, **145**, 257.

[3] *Ibid.* **192**, 106.

[4] Berichte, **12**, 2282.

One of the most remarkable cases of intermolecular rearrangement is the conversion of hydrazobenzene into two isomeric diamidodiphenyls by the action of dilute mineral acids. This reaction is probably intimately connected with the marked tendency of the weak basic — NH — NH — group to take up hydrogen and pass over into strong basic amido groups; thus, hydrazobenzene, when heated, decomposes into aniline and azobenzene. The primary action of chlorhydric acid on hydrazobenzene is to form an unstable salt, probably $\begin{array}{ll} C_6H_5 - & NHHCl \\ & \mid \\ C_6H_5 & NHHCl \end{array}$. The salt is then decomposed into $C_6H_5NH_2$ and Cl, and the chlorine acts on one of the hydrogen of C_6H_5, forming $C_6H_4 - NH_2HCl$, two molecules of which go over into $\begin{array}{l} C_6H_4NH_2HCl \\ \mid \\ C_6H_4NH_2HCl \end{array}$. It is more likely that the two reactions occur simultaneously, and it is not only a consequence of the affinity of the NH — NH group for hydrogen, but also of chlorine for the hydrogen of the phenyl group. The formation of two isomeric diamidodiphenyls is due to the chlorine acting on hydrogen atoms in the ortho and para-positions toward the NH group.

V. Meyer has recently shown that nitrous acid acts on the hydrogen of a methylene group, when the carbon is united with certain negative radicals, replacing it by N — (OH). This observation may be used to explain the action of nitrous acid on primary amines. The first product of the action of nitrous acid on aniline nitrate should be ${}^{C_6H_5}_{\;H}\!>\!N\!<^{N(OH)}_{ONO_2}$, but the compound $C_6H_5 - N - N(OH)$ has not the property of combining with acids to form a substituted ammonium salt, a decomposition into $C_6H_5 - N - N(OH)$ and nitric acid therefore takes place. Diazobenzene behaves, however, toward acids like a strong base; the nitric acid, therefore, reacts on it, forming diazobenzenenitrate and water. In the paraffin series the reaction is probably of the same nature, only the instability of the new product is so great that a decomposition into an alcohol and nitrogen takes place at ordinary temperature. This is in accordance with the greater affinity of unsaturated carbon for elements than saturated carbon for the same elements. If $CH_2 - CHNH_2$ were known, it would probably yield a diazo compound that could be isolated.

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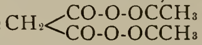
[1] Annalen der Chemie, **180**, 88; **188**, 91.

IX.—ON A NEW SYNTHESIS OF CINNAMIC ACID.

Several years ago[1] I showed that by heating mixtures of benzoic, salicylic or cuminic aldehydes with sodium acetate and phenylacetic acid, stilbene and substituted stilbenes can be obtained. From succinic acid and benzoic aldehyde a well-defined product could not be obtained. Recently this reaction has been tried with malonic acid. A mixture of malonic acid, benzoic aldehyde, in proportion of their molecular weights, and $\frac{1}{3}$ part fused sodium acetate, heated in a closed tube for several hours at 140°, gave a very good yield of cinnamic acid:

$$C_6H_5CHO + CH_2(COOH)_2 = C_6H_5 - CH - CH - COOH + CO_2 + H_2O.$$

It is not necessary, however, to add sodium acetate to the mixture. Benzoic aldehyde and malonic acid, heated for several hours in a closed tube at 130°, gave a satisfactory yield of cinnamic acid. Fittig[2] infers from the results of his recent experiments on the action of benzoic aldehyde on sodium succinate and acetic anhydride, that in Perkins' reaction the condensation, or carbon-polymerisation, occurs between the salt and the aldehyde, and not between the anhydride and the aldehyde, as was formerly supposed. It seems to me that his results do not permit such a generalisation. It is extremely probable that the product of the action of acetic anhydride on sodium succinate contains, according to the conditions, either a mixed succinic-acetic anhydride, or a mixture of acetic and succinic anhydrides, sodium acetate and succinate. The aldehyde will act on the hydrocarbon group whose hydrogen are the most exposed to the loosening influence of oxygen; in the present instance undoubtedly the methylene of succinic anhydride. Halogens act with difficulty on acetic acid, readily on acetic anhydride; the latter compound is used in Perkins' reaction, whereas the first cannot be used. The reason of the greater reactive properties of the hydrogen of acetic anhydride is to be sought in loosening effect of oxygen on the affinity of carbon for hydrogen. In acetic acid the influence of oxygen has been, in comparison with the anhydride, partly neutralised by a partial replacement of oxygen by hydrogen. In sodium acetate the loosening influence of oxygen is again decreased, in comparison with acetic acid, owing to the introduction of a more positive element in the place of hydrogen; this is exactly the reverse of what Fittig infers from his results. The experiments of this chemist on the action of benzoic aldehyde, acetic anhydride and sodium malonate, do not prove his views. If the mixed anhydride  $CH_2 <\begin{matrix} CO\text{-}O\text{-}OCCH_3 \\ CO\text{-}O\text{-}OCCH_3 \end{matrix}$ is formed, it is evident that the reaction will take place between the CH_2 group and formyl; not to mention that, as the above-described experiment shows, if the affinity of hydrogen for carbon is sufficiently loosened the action of heat alone suffices to effect a condensation. I do not intend to enter into the application of these views to the results of Perkin's, Oglialoro's, Fittig's, and my own experiments; but they offer an explanation for the apparently contradictory results, to which Fittig and others have already called attention. The influence of the oxygen on the properties of organic compounds containing it has not had the general consideration which the subject merits. I shall reserve the theoretical consideration of this subject, as well as the description of a series of experiments now in progress, for a separate paper; and only mention here that it offers a satisfactory explanation for the general form which Gabriel and myself[1] have given to Markownikoff's rule, for Popoff's rule for the oxidation of ketones, and for other equally important facts.

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[1] This Journal, **1**, 312.

[2] Annalen der Chemie, **216**, 115.

TUFTS COLLEGE, MASS., June 20th, 1883.

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 1016.

ESTIMATION OF SULPHUR IN ORGANIC COMPOUNDS.

By E. H. Keiser.

Of the many methods devised for the estimation of sulphur in organic substances, Liebig's process for non-volatile compounds is the simplest and most expeditious. As ordinarily carried out, 20–25 grams of potassium hydroxide and 4–5 grams of potassium nitrate are fused in a silver crucible or dish. The fused mass is allowed to cool and a weighed quantity of the substance added. The crucible is then heated, and the contents stirred with a silver spatula until all the carbon is oxidised and the fused mass becomes perfectly transparent. After cooling it is dissolved in water, the solution acidified with hydrochloric acid, and the sulphuric acid precipitated with barium chloride. The weight of barium sulphate thus obtained is generally too high, and it is necessary to purify it by reprecipitation. The chief source of error by this method is due to the fact that the fused potassium hydroxide and nitrate take up an appreciable quantity of silver from the dish or crucible, and, on acidifying with hydrochloric acid, the silver chloride formed is held in solution by the excess of potassium chloride present, and is then carried down by the barium sulphate, thus increasing the weight of the precipitate.

Various attempts have been made to improve the method. Potassium hydroxide alone has been used to fuse the substance with, and the solution treated with bromine to complete the oxidation.[1] But even in this case the fused hydroxide takes up silver, which is afterwards converted into bromide and carried down by the barium sulphate. Besides, certain compounds, such as naphthalene-sulphamide, are oxidised only very slowly by fused potassium hydroxide, and for complete oxidation by this method require protracted heating with a large quantity of alkali.

Accurate results may be obtained, without reprecipitating the barium sulphate, by the following modification of Liebig's method:

Ten grams of caustic potassa, free from sulphur, are fused in the silver crucible and allowed to cool. The weighed substance (0.1—0.3 gram) is then added, and the crucible heated until the contents have become thoroughly mixed. One gram of the crystallised potassium nitrate is then added and the heating continued until the fused mass has become perfectly transparent. The crucible is allowed to cool and the contents dissolved in distilled water. The solution is neutralised with hydrochloric acid. It becomes perfectly clear, but if allowed to become cold and then be diluted with a large volume of water ($\frac{3}{4}$—1 litre), all the silver chloride is precipitated. After allowing the precipitate to settle the solution is filtered, and in the filtrate the sulphuric acid is determined in the usual way by precipitation with barium chloride. The following results were obtained by this method:

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[1] Fahlberg and Iles. Berichte der deutschen chemischen Gesellschaft, **11**, 1187.

I. 0.2556 gram sulphamine-metatoluic acid gave 0.2775 gram $BaSO_4 = 14.90$ per cent. sulphur.

II. 0.1045 gram sulphamine-metatoluic acid gave 0.1127 gram $BaSO_4 = 14.81$ per cent. sulphur.

III. 0.1847 gram of sulphamine-metatoluic acid gave 0.1990 gram $BaSO_4 = 14.78$ per cent. sulphur.

	Calculated for $C_8H_9SNO_4$.	Found.		
		I.	II.	III.
S	14.88	14.90	14.81	14.88

IV. 0.2111 gram β-naphthalene-sulphamide gave 0.2364 gram $BaSO_4 = 15.38$ per cent. sulphur.

V. 0.1371 gram β-naphthalene-sulphamide gave 0.1547 gram $BaSO_4 = 15.49$ per cent. sulphur. Calculated for $C_{10}H_9SNO_2$ 15.46 per cent.

		Found.	
		IV.	V.
S	15.46	15.38	15.49

VI. 0.1396 gram taurine gave 0.2611 gram $BaSO_4 = 25.67$ per cent. sulphur. Calculated 25.60 per cent. sulphur for $C_2H_7NSO_3$.

VII. 0.2464 gram para-dipropyl-benzene-sulphamide gave 0.2399 gram $BaSO_4 = 13.37$ per cent. sulphur. The formula requires 13.27 per cent.

VIII. 0.2852 gram para-propyl-sulphamine benzoic acid gave 0.2773 gram $BaSO_4 = 13.35$ per cent. sulphur. The formula $C_{10}H_{13}NSO_4$ requires 13.17 per cent. sulphur.

Dr. W. C. Day obtained by this method the following results:

I. 0.2138 gram cymene-sulphamide gave 0.2304 gram $BaSO_4 = 14.79$ per cent. sulphur.

II. 0.2824 gram cymene-sulphamide gave 0.3045 gram $BaSO_4 = 14.80$ per cent. sulphur. The formula $C_{10}H_{15}NSO_2$ requires 15.02 per cent. sulphur.

Chemical Laboratory, Johns Hopkins University, June, 1883.

Communications from the Chemical Laboratory of Rutgers College.

X.—AMMONIUM FERROUS SULPHATE AS A REAGENT FOR NITRIC ACID.

By Peter T. Austen and J. Chester Chamberlain.

The easy oxidisability of ferrous sulphate renders it impossible to keep a solution of it as a laboratory reagent; and although methods have been suggested for preserving it—as, for instance, covering the surface with a layer of petroleum—the solution is still generally made only when it is needed.

A solution of ammonium ferrous sulphate, which can now be easily obtained, answers excellently in place of the ferrous sulphate, and has the advantage of being permanent, so that it can be used as a desk reagent. A solution of convenient strength can be made by dissolving 200 grams of the double salt in a litre of water containing about 20 cc. of concentrated sulphuric acid. The solution can easily be made, when the double salt is not obtainable, by dissolving one molecule of ferrous sulphate and one molecule of ammonium sulphate in water containing one or two per cent. by volume of concentrated sulphuric acid. Sufficient amounts of the salts are taken to give a solution containing about twenty per cent. of the double salt.

A convenient solution is made by dissolving 12 grams of ferrous sulphate and 6 grams of ammonium sulphate in 100 cc. of water containing 2 cc. of concentrated sulphuric acid. A slight excess of sulphuric acid seems to have a beneficial effect in making the solution keep. A solution of this kind, after standing in a closed bottle for three months, gave the test with sharpness, and three weeks' exposure in a loosely-covered wide beaker did not injure its powers.

A series of experiments was made to ascertain if the double salt was as delicate a test as the ferrous sulphate alone. A solution of potassium nitrate containing 0.001 gram of NO_3 gave a distinct ring at once, while a solution containing 0.0001 gram of NO_3 gave a perceptible ring on standing three hours. These results were, if anything, more delicate than those obtained with ferrous sulphate alone.

New Brunswick, N. J.

XI.—THE ANALYSIS OF STANNATE OF SODA.

By Peter T. Austen.

The usual method of determining the amount of stannic oxide in sodic stannate is by adding dilute sulphuric acid to the hot solution until it is faintly acid, and then filtering off and washing the gelatinous precipitate of stannic hydroxide. The determinations are, as a rule, quite satisfactory, but the precipitate is very gelatinous and slow to wash.

It occurred to me that the precipitation of stannic nitrate by heat might be applied to the analysis of stannate, and that, as the liquid in this case is strongly acid, the filtration and washing would be easier. It was found that when stannate of soda was acidified with strong nitric acid, a clear solution was obtained from which, when heated to boiling, all the tin was precipitated. In no case could a trace of tin be detected in the filtrate by hydrogen sulphide. The precipitate is flocculent and gelatinous, but not quite so much so as the precipitate of stannic hydroxide obtained by acidifying a solution of the stannate.

The precipitate formed on heating a stannic nitrate solution is insoluble in nitric acid. It is soluble in concentrated chlorhydric acid, and the precipitate formed by adding potassium carbonate to this solution is not redissolved in excess. From this it is to be inferred that the precipitate is metastannic acid, and not stannic hydroxide, as generally stated.

The precipitate is more easily filtered and washed than that of stannic hydroxide. In the following analyses commercial liquid stannate of soda was used. The weighed portion was washed into a beaker with water, using about 25 cc. Concentrated nitric acid was then added drop by drop, while shaking, till a clear solution was obtained. The solution was diluted to about 250 cc. and heated to boiling. After the precipitate had formed, the liquid was well stirred and then allowed to settle. The clear liquid was decanted on a filter, and the precipitate washed a few times with hot water by decantation, then transferred to the paper, and the washing continued until the washings were free from acidity by test paper. The paper and precipitate were dried, incinerated and heated for two or three minutes over the blast-lamp. Solid stannate of soda is analysed in the same way, a water solution of it being made in the usual manner.

Weight Taken.	Per cent. of SnO_2.
6.2122	8.94
5.0531	8.92
7.0162	8.91
By precipitation with dil. sulphuric acid.	
6.0822	9.08[1]
6.6032	8.95

NEW BRUNSWICK, N. J.

REVIEWS AND REPORTS.

ANALYTICAL CHEMISTRY.

A new method of estimating the Halogens in Volatile Organic Compounds.[2] The method now almost exclusively employed for estimating the halogens in organic compounds is that of Carius, which consists in heating the substance in a sealed tube with fuming nitric acid and silver nitrate. R. T. Plimpton and E. E. Graves propose a substitute for this, in the case of volatile compounds. The substance is introduced into a U tube through which illuminating gas and air are passed, as in a Bunsen burner. The volatile substance evaporates and burns with the gas at a tip on one end of the tube, the halogens being left partly free and partly in combination with hydrogen. The evaporation is sometimes aided by warming the tube with hot water, or otherwise. The temperature is raised or lowered so that the substance may always be detected in the flame, and yet not in sufficient quantity to make the flame luminous. The products of combustion are aspirated through a bent funnel tube and collected in dilute caustic soda; this is boiled with sulphurous acid to reduce chlorates, etc., and then the halogens precipitated with silver nitrate. The success of the experiment depends upon the regular volatilisation of the compound; if this is unduly hurried the flame becomes luminous, and the combustion may be incomplete. On the other hand, the evaporation should not be too slow, or, before it is complete, the caustic soda in the absorbing tubes will become saturated with carbonic acid.

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[1] This precipitate was not quite washed out.

[2] Journal of the Chemical Society, March, 1883, 119.

Hydrogen dioxide in Analytical Chemistry. The discovery of the valuable disinfectant properties of hydrogen dioxide has led to its manufacture on the large scale. It is now sold in the form of a 2—3 per cent. solution in water. A few preliminary experiments have shown that this solution is a powerful and convenient oxidising agent, which must replace nitric acid, bromine and chlorine to a considerable extent, and its use has also been proposed in the larger bleaching industries. A. Classen and O. Bauer[1] now call attention to a scheme by which hydrogen dioxide may be used as a laboratory reagent, particularly in quantitative analysis. The solution just mentioned is not sufficiently pure for analytical purposes; it contains alumina, and, further, is acidified with sulphuric acid, to prevent decomposition, and this would interfere with its use in sulphur determinations. But a solution prepared in Berlin especially for analytical purposes is quite pure, and can be obtained acidified with either hydrochloric or sulphuric acid. It is known that hydrogen dioxide oxidises arsenious acid to arsenic acid, and phosphorous to phosphoric acid; and, further, that it decomposes hydrogen sulphide, forming water and free sulphur,

$$H_2O_2+H_2S=2H_2O+S.$$

But the latter reaction does not take place if the hydrogen dioxide acts in *ammoniacal solution*, *i. e.* on ammonium sulphide. If this substance or sodium sulphide is treated with hydrogen dioxide the liquid becomes warm, and is gradually decolorised without deposition of sulphur. The latter is oxidised to sulphates and hyposulphites. If the liquid is heated, after adding hydrogen dioxide, sulphates alone are formed. By passing hydrogen sulphide through a solution of hydrogen dioxide made strongly alkaline with ammonia, sodium carbonate or caustic potassa, it is completely oxidised to sulphates. No less interesting is the conduct of solutions of sulphides of tin, antimony and arsenic in ammonium sulphide: on adding hydrogen dioxide gradually, the ammonium sulphide is oxidised, causing at first a precipitation of the other sulphides; but by adding an excess of the reagent and heating, tin sulphide is transformed completely into the insoluble oxide, and antimony partly into insoluble oxide and partly into a soluble compound. Arsenic sulphide, however, is transformed completely into salts of arsenic acid. By acting on sulphide of sodium and tin, the latter goes partly or completely into solution, according to the proportion of sulphide of sodium.

The above conduct of hydrogen dioxide towards ammonium sulphide, or the action of hydrogen sulphide gas on ammoniacal hydrogen dioxide, may be applied in qualitative analysis for destroying an excess of these compounds, and in quantitative analysis for determining amounts of gaseous or dissolved hydrogen sulphide, or for the determination of sulphur or metals in sulphides. In cases where the sulphide can be decomposed by the direct action of hydrogen dioxide in presence of ammonia, it is done in this way; in other cases, where heating the sulphide with hydrochloric acid causes the evolution of a definite amount of hydrogen sulphide, the latter is oxidised by hydrogen dioxide and estimated as barium sulphate. Sulphites are likewise completely oxidised to sulphates, and this reaction may be used in several ways for analytical purposes.

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[1] Berichte der deutschen chemischen Gesellschaft, **16**, 1061.

The sulphides of arsenic, copper, zinc and thallium are oxidised without the formation of a precipitate. In the case of copper, after the oxidation is complete and the excess of ammonia driven off, the copper is all left as a green insoluble powder which is not altered by ignition; by treating sulphide of zinc in a similar manner only part is obtained as a white precipitate, the rest going into solution. By the action of hydrogen dioxide on antimony trisulphide part of the antimony is precipitated as oxide, but in all these cases the liquid contains all the sulphur as sulphuric acid. Hydrogen dioxide acts in various ways on the other metallic sulphides. It attacks mercury sulphide energetically, although this is hardly changed with nitric acid. After driving off the ammonia the mercury is all found in a spongy precipitate.

Sulphide of cadmium is similarly transformed into a light yellow precipitate, but after complete oxidation a portion of the cadmium is also found in solution as sulphate. Some metallic sulphides, which can be precipitated by ammonia from their solutions in acids, are decomposed by ammoniacal hydrogen dioxide, with the formation of sulphuric acid and precipitation of the metals as hydroxides. Sulphides of iron and manganese are quickly oxidised in this way. By heating cobalt sulphide with ammoniacal hydrogen dioxide, cobalt sulphate is first formed, which is partly converted into a brown precipitate on further heating. Sulphide of nickel yields a green precipitate which does not contain all of the metal. Sulphides of silver and bismuth are not completely decomposed. Sulphide of lead is easily oxidised to sulphate.

With these preliminary statements as to the action of hydrogen dioxide on the metallic sulphides, the following are the analytical processes to which it is applied: The property of oxidising hydrogen sulphide in alkaline solution easily and completely to sulphuric acid, may be taken advantage of in the estimation of chlorine, bromine and iodine in liquids containing hydrogen sulphide. In the case of chlorine an ammoniacal solution of hydrogen dioxide is added to the liquid containing the chloride and hydrogen sulphide, and this is boiled until the complete decomposition of hydrogen dioxide is shown by no more oxygen being evolved. The chlorine is then precipitated with silver nitrate in the usual way. When bromine or iodine is to be determined, the hydrogen dioxide is made alkaline with sodium carbonate. If an ammoniacal solution is used, ammonium nitrite is formed, which is decomposed on acidifying and causes the liberation of free bromine or iodine.

As indicated above, metallic sulphides which are oxidised directly by hydrogen dioxide may be estimated by determining the amount of sulphuric acid formed in the oxidation. This method is applicable for the estimation of arsenic, antimony, zinc, copper and cobalt. The authors have shown by special experiments that all the arsenic is oxidised to arsenic acid, which they determine as ammonium magnesium arsenate. Antimony trisulphide is oxidised completely by hydrogen dioxide, but the pentasulphide is not completely oxidised. The principle of estimating hydrogen sulphide evolved by hydrochloric acid from such metallic sulphides as are decomposed by this means, has been in use for some time, a solution of bromine being used to oxidise the hydrogen sulphide. But the objectionable properties of bromine on the one hand, and the fact that all excess of it, as well as hydrochloric acid, must be gotten rid of before precipitating the sulphuric acid, and further, the frequent precipitation of sulphur during the process, are reasons enough for the use of the hydrogen dioxide solution in its stead, especially as it contains nothing which interferes with the direct precipitation of the sulphuric acid. The estimation of metals by this means is capable of more extended application than the direct oxidation of the sulphide. Pure metallic sulphides are seldom obtained in analyses, but more frequently mixtures with free sulphur.

The estimation of antimony and tin in these mixtures is a difficult matter and always requires considerable time. But the amount of free sulphur does not affect the quantity of hydrogen sulphide liberated by an acid, and hence the advantage of determining the latter. It is absorbed in a peculiar apparatus, described in full by the authors. Foremost among the metals that may be conveniently determined in this way are antimony, tin, cadmium and iron. When antimony trisulphide is treated with hydrochloric acid, under the proper conditions, it yields three molecules of hydrogen sulphide,

$$Sb_2S_3+6HCl=2SbCl_3+3H_2S.$$

Antimony pentasulphide is decomposed with liberation of the same amount of hydrogen sulphide and deposition of sulphur,

$$Sb_2S_5+6HCl=2SbCl_3+3H_2S+2S.$$

As far as the estimation of the antimony is concerned, it is immaterial whether it is in the form of tri- or pentasulphide or a mixture of both, for three molecules of hydrogen sulphide always represent two atoms of antimony.

Sulphites may be determined in the same way as sulphides. If the sulphite is free from sulphate it may be oxidised with hydrogen dioxide directly; but if sulphuric acid is present, the sulphurous acid is evolved and then oxidised as usual. The method allows of the estimation of a hyposulphite, sulphite and sulphate in the same liquid. By boiling with an acid the sulphurous acid of the sulphite and hyposulphite is liberated and determined. The sulphur, precipitated from the hyposulphite during this process, is filtered off and weighed, this gives the amount of hyposulphite originally present. Finally the sulphuric acid is precipitated as barium sulphate.

The Substitution of Ammonium Hyposulphite for Hydrogen Sulphide in the general course of Qualitative Analysis.[1] — A. Orlowsky has found by his investigations on the action of ammonium or sodium hyposulphite on solutions of the ordinary metals, that, 1. All metals that can be precipitated by hydrogen sulphide in acid solutions are also precipitated by ammonium or sodium hyposulphite, from a boiling solution acidified with hydrochloric acid. Lead alone furnishes an exception, inasmuch as it remains in solution together with a portion of the cadmium, if the solution is very acid. 2. The metals thus precipitated may be divided into two classes by means of alkaline sulphides. 3. Metals which are not precipitated by hydrogen sulphide from an acid solution are not precipitated by hyposulphites. 4. The salts of the alkaline earths, however, conduct themselves toward hyposulphites in a manner entirely different from that exhibited with hydrogen sulphide and ammonium sulphide. In neutral or alkaline solutions, hyposulphites of the alkaline earths are formed, which are precipitated from acid solutions by ammonia. By continued boiling the hyposulphites of the alkaline earths are decomposed into sulphates and sulphites. Ammonium or sodium hyposulphite may be used, therefore, for the detection and also for the separation of metals. In applying them to the general course of separation of metals, Orlowsky proceeds as follows: Lead, barium, strontium and part of the calcium, are first separated from the solution by ammonium sulphate, and detected in the ordinary way. The filtrate, which must not contain nitric acid, is acidified with hydrochloric acid and heated to boiling, then it is treated gradually with sodium or ammonium hyposulphite, warming and shaking thoroughly between the additions. The liquid must remain acid to the end of the reaction. The precipitate may contain sulphides of antimony, arsenic, tin, gold, platinum, mercury, silver, copper, bismuth, and cadmium. These may be further treated with ammonium sulphide. The filtrate is neutralised with ammonia and precipitated as usual with ammonium sulphide, by which, however, cadmium may be in the precipitate, and will be found further on with the zinc and manganese. In the last filtrate antimony and tin must be sought for as well as the alkalies and calcium and magnesium, since these metals like cadmium are not completely precipitated from acid solution by ammonium hyposulphite.

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[1] Journal der russ. phys. chem. Gesellschaft, 1883, 32, and Berichte der deutschen chemischen Gesellschaft, **16**, 807.

Nitrogen.—As a general method for the determination of nitrogen, H. Gronnen[1] recommends burning the nitrogenous substance in a slow current of superheated steam. The substance is placed in a wrought-iron tube containing fragments of a peculiar kind of clay. This tube is connected with another in which steam is generated; both are enclosed in a peculiar charcoal furnace and heated to bright redness. The nitrogen is all converted into ammonia, which is absòrbed and estimated as in soda lime process. The method is applicable for determining nitrogen in food, vegetables containing nitrates, guano and ammoniacal superphosphates, and also for commercial saltpetre. In the latter case sugar is added to the substance, so that carbon will be present to decompose water and liberate hydrogen, with which the nitrogen forms ammonia.

Phosphorus.—The determination of phosphoric acid by the molybdenum method,[2] by Ernst Täuber. The results of this series of investigations are, in the main, confirmations of the views of Stünkel, Wetzke and Wagner, and Maercker; and are in brief as follows:

1. The presence of large amounts of ammonium nitrate is advantageous when phosphoric acid is precipitated from nitric acid solutions by molybdenum solutions. It hastens the precipitation, renders a great excess of molybdic acid unnecessary, and gives the precipitate a loose, spongy character.
2. The precipitate of ammonium phospho-molybdate may be washed with a solution of ammonium nitrate.
3. Magnesium mixture must be added slowly, with stirring, to the ammoniacal phosphate solution.
4. Igniting the magnesium pyrophosphate with a blast lamp is unnecessary for the usual cases of analysis.

Chromium.—Chalmers Harvey[3] proposes a method for the volumetric estimation of chromic acid in chromates and bichromates analogous to his method for the analysis of manganese dioxide.[4] The chromic acid is reduced by heating with a known amount of stannous chloride in excess, and this excess titrated with a standard solution of ferric chloride. Determinations can be made in a few minutes, and the results given are quite accurate; but a manifest objection to the method is, that the solution of stannous chloride is liable to change; and, further, it is not easy to prepare a solution of ferric chloride free from both ferrous chloride and chlorine.

A New Reaction of Aldehydes.—F. Penzoldt and Emil Fischer[5] have found that by mixing grape sugar with an alkaline solution of diazobenzene-sulphonic acid a red color is produced after 10–15 minutes, and this gradually changes to a violet. Acetaldehyde gives the same reaction, but the color is not produced under the above conditions with the more stable aromatic aldehydes. It may be produced easily, however, by an addition of sodium amalgam. By use of the latter the reaction is also hastened and increased in the case of grape sugar and acetaldehyde. The reaction is so characteristic that it appears particularly adapted for the detection of aldehydes. The test is best conducted with pure crystallised diazobenzene-sulphonic acid. It is dissolved fresh each time in about 60 parts of cold water with a little dilute caustic soda. The substance to be tested is added, mixed with dilute alkali, and then a small piece of sodium amalgam, and allowed to stand quietly. If an aldehyde is present, the reddish violet color, similar to pure fuchsine, appears in 10–20 minutes. The test is much more delicate than the reaction with fuchsine-sulphurous acid. Oil of bitter almonds may be detected with certainty in a dilution of 1 part in 3000. Neither chloral nor benzoïn gives the reaction, and acetone and acet-acetic ether give under like conditions a dark red color without the characteristic violet tinge. The same is true with phenol, resorcin, and pyrocatechin, if care is taken to have an excess of alkali present to prevent the formation of the known azo-dyes.

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[1] Die landwirthschaftlichen Versuchs-Stationen, **28**, 343.

[2] *Ibid.* **28**, 333.

[3] Chemical News, **47**, 86.

[4] *Ibid.* **47**, 2.

[5] Berichte der deutschen chemischen Gesellschaft, **16**, 657.

Litmus, methyl-orange, phenacetolin and phenol-phthaleïn as indicators.—Robert T. Thomson[1] has made a series of comparisons of these indicators for the purpose of determining the relative degree of sensitiveness of which each is capable, both in solutions containing only pure acids or alkalies, and also when various impurities are present. The tests were made in such a way that the solution employed would measure about 100 cc., when the end reaction was observed. The strengths of the indicator solutions were so arranged that equal volumes of each gave about the same intensity of color at the point at which the change, caused by excess of acid or alkali, was just complete. 0.5 cc. was used in each experiment. When no interfering substance was present the indicators all gave quite sharp results, phenol-phthaleïn requiring somewhat less standard alkali for bringing out its characteristic color than did the others. In determining the alkalinity of caustic soda containing some sodium carbonate, methyl-orange lost somewhat in sharpness, this being due to the presence of the neutral salt formed in the reaction. Phenacetolin may be used to determine the amount of hydroxide and carbonate in commercial caustic soda, but if the proportion of carbonate is considerable the reaction is not sharp. Phenol-phthaleïn can be used for the above purpose very readily, for it loses its alkaline indication when all the sodium hydroxide has been neutralised and the carbonate converted into acid carbonate. On decomposing the acid carbonate by boiling, the red color reappears, and thus the amount of carbonate may be determined. Phenol-phthaleïn does not give good indications in the presence of ammonium salts. Litmus and phenacetolin are quite as delicate in the presence of sulphates, nitrates and chlorides of sodium, potassium and ammonium. When these salts were tested with the volume of methyl-orange used in the foregoing experiments it was found that about 0.2 cc. of normal acid was required to bring out the full pink color, against 0.05 cc. when distilled water only was employed, although a distinct change was produced in the former case. The delicacy of phenol-phthaleïn is not affected by the salts of sodium and potassium mentioned above, but quantities of sulphate, nitrate and chloride of ammonium equivalent to 0.85 gram of ammonia per 100 cc., required about 1.5 cc. of normal caustic soda to produce even the faintest red color, showing that ammonia and its salts must be carefully excluded when this indicator is made use of. Sulphites of the alkalies are alkaline with litmus, methyl-orange and phenacetolin, until half the sulphite has been neutralised. Phenol-phthaleïn is practically neutral with sulphites. With sulphides the liberation of sulphuretted hydrogen, on adding a standard acid, does not affect methyl-orange, but with the other indicators the hydrogen sulphide must be boiled off in order to estimate all of the sulphide. Statements are also made as to the phenomena accompanying the titration of phosphates, silicates, nitrites, borates, oxalic, tartaric, citric, and the ordinary mineral acids.

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[1] Chemical News, **47**, 123, 135, 184.

Phenol-phthaleïn.—N. Menschutkin[1] has shown that the alkaline reaction of triethylamine with phenol-phthaleïn is destroyed by alcohol. When water, containing a few drops of phenol-phthaleïn solution, is treated with triethylamine it is colored purple violet. An aqueous solution of triethylamine shows a strong alkaline reaction. If, now, alcohol is added the color becomes paler, and disappears when two volumes of 95 per cent. alcohol have been added. On the other hand, if phenol-phthaleïn is added to alcohol, and then triethylamine, there is no violet coloration. The alkalinity of the triethylamine has disappeared. Alcohol destroys the compound of phenol-phthaleïn with triethylamine, even with a great excess of the latter. The color that has been destroyed by alcohol is restored by the addition of an alkali, but it is not as intense as the aqueous solution. Similarly the color given to phenol-phthaleïn by ammonia is destroyed by the addition of three volumes of alcohol. The author has used this reaction for distinguishing between ammonia and free alkalies in the same solution. D. T. D.

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[1] Berichte der deutschen chemischen Gesellschaft, **16**, 319.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

(*Continued from* **4**, 468.)

METABOLISM.

Formation of Urea.—The place where urea is formed in the body has been for some time more or less of an open question. Recently W. v. Schroeder[1] has obtained positive results by a series of experiments, in which a current of blood was made to circulate through living organs, the amount of urea in the blood being determined both before and after it had passed through the organ in question. The method employed in the determination of the urea was a somewhat novel one, being a combination of Liebig's and Bunsen's method. 100 cc. of blood were precipitated with five times its volume of absolute alcohol, filtered after standing twelve hours, and the filtrate evaporated to dryness at a temperature not exceeding 75° C. The residue was dissolved in water, and the solution, which filters very slowly, clarified by the addition of a little alum solution and an excess of baryta water, followed by precipitation of the baryta with carbonic acid. The filtrate was precipitated with mercuric nitrate, from which the urea was separated by hydrogen sulphide, and the solution heated in a sealed tube with an ammoniacal solution of barium chloride. The barium carbonate thus obtained was not weighed, but the carbonic acid was liberated by citric acid and then measured. The accuracy of the method was proved by control experiments.

After a preliminary experiment with a dog, which confirmed the accumulation of urea in the blood after extirpation of the kidneys, v. Schroeder made an injection experiment with an ox kidney, in which ammonium carbonate was added to the blood. The content of urea in the blood was not at all increased. Similar experiments with dogs' kidneys led to a like result. Thus, in one experiment the amount of urea in the blood was .0140 per cent. before the injection, while after the injection it was .0137 per cent. In a second experiment the blood before the injection contained .0384 per cent. urea; afterwards, .0372 per cent. It is thus apparent that neither the kidneys nor the muscles, which during the experiments retain their excitability, are capable of converting ammonium carbonate into urea. Further experiments were made with the livers of dead dogs, two always being used, the smaller furnishing the liver, while the blood of both, about one litre, served for the injection. The blood was introduced into the portal vein and taken out from the vena cava above the diaphragm, the hepatic artery being ligatured. In one experiment the entire quantity of blood (1250 cc.) was passed through the liver three times, and then a sample taken for analysis. The remaining 1000 cc. were passed through the liver during 3¾ hours twenty times, altogether .16 gram of ammonia being added in the form of ammonium carbonate. The blood prior to the injection contained .0442 per cent. urea; after the injection .0812 per cent., while the solid matter had only very slightly increased. In a second experiment the amount of urea increased from .0538 per cent. to .1253 per cent. To guard against the possibility of the blood in its passage through the liver taking up substances other than urea which would furnish carbonic acid by heating, v. Schroeder made an experiment with the liver of a hungry dog, without the addition of ammonium carbonate to the blood. There was no appreciable difference in the content of urea before and after the injection. An increase of urea, however, was noticed when the liver of a dog in full digestion was employed. In this case the content of urea in the blood rose from .0499 per cent. to .0636 per cent. without the addition of ammonium carbonate—that is to say, the liver possesses the power of converting into urea some antecedent substance formed during digestion. In one experiment 1.184 grams of urea were formed during 4 hours. If, therefore, 30–40 litres of blood could pass through the liver of a living dog weighing 15 kilos in one hour, 30–40 grams of urea would be formed during the 24 hours; from which it would appear that the entire quantity of urea excreted during one day could be formed in the liver. Regarding the theory of its formation, v. Schroeder holds that the ammonium carbonate passes directly into urea by a withdrawal of water.

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[1] Archiv f. exp. Path. **15**, 364. Also Centralbl. f. med. Wiss. 1883, 84.

Further contributions to our knowledge concerning the formation of urea have been recently made by E. Salkowski,[1] who has studied the behavior of several amido acids in the animal body. Amidobenzoic acid was first studied with a view to ascertain whether it passed into uramidobenzoic acid in the organism, an idea contradictory to the earlier researches of Schultzen and Graebe,[2] according to whom the amidobenzoic acid should form amidohippuric acid. In his experiments Salkowski used metamidobenzoic acid, which was given to rabbits and dogs in quantities of 2 to 10 grams per day in the form of a sodium salt. In the urine uramidobenzoic was found in sufficient quantity for analysis and to thoroughly establish its identity. In the case of rabbits 5 per cent. was obtained as uramidobenzoic acid, and in the case of dogs nearly 20 per cent. Thus by carnivorous as well as by herbivorous animals, and also by the human body, a definite quantity of uramidobenzoic acid is formed from amidobenzoic, thus furnishing a new example for the addition of cyanic acid to those already known in the body; since as yet, under the conditions which prevail in the animal organism, no other mode of formation of uramido acids is known than the addition of cyanic acid. For the herbivorous animals, as Salkowski[1] remarks, this fact is not without value. This investigator had previously shown the formation of uramidobenzoic acid by rabbits, and for a long time this remained the only example of uramido acid formation by herbivorous animals, until Blendermann[2] proved the addition of cyanic acid to tyrosin in the rabbit. From the observations of Jaarsveld and Stokvis,[3] and even more from those of Schmiederberg[4] on the decomposition of hippuric acid in the body, it might be supposed that a considerable quantity of uramidobenzoic would be formed, not however to be excreted as such, but further decomposed. Against the correctness of this latter view Salkowski finds that even small quantities of uramidobenzoic acid introduced into the body are found again in the urine. Again, Salkowski has endeavored to ascertain, by feeding experiments on dogs and rabbits, the influence of amidobenzoic acid on proteid metabolism. His results tend to show that the excretion of urea is increased under the influence of this acid, but at the same time a larger quantity of albumin is decomposed, which furnishes the necessary amount of nitrogen for the formation of uramidobenzoic acid. The production of urea is, however, not dependent on the formation of the latter acid; it goes on quite independent of this. In regard to where uramidobenzoic acid is formed, Salkowski found that after extirpation of the kidneys of a rabbit, the acid was present in the blood, liver and muscles, after amidobenzoic acid had been given. After ligaturing the ureters, the amount of acid found in the organs was not increased, so that it is plainly apparent that the formation of uramidobenzoic acid does not take place in the kidneys; and since v. Schroeder has found that the change from ammonium carbonate to urea takes place in the liver, it is quite probable that the former change also takes place there.

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[1] Zeitschrift für physiologische Chemie.

[2] Annalen d. Chem. u. Pharm. **142**, 354. See this Journal, **2**, 270.

There are now, as Salkowski remarks, four amido acids, viz. sarcosine, taurine, tyrosine and amidobenzoic, which illustrate the formation of uramido acids. These substances appear in the urine partly as uramido acids and partly as anhydrides. Only a portion of the substance is concerned in the reaction, and the behavior of the individual amido acids is exceedingly variable, being probably dependent upon the behavior of this residue. Thus as decomposition products of tyrosine Brieger[5] has discovered phenol, Blendermann[6] oxyhydroparacumaric acid and tyrosinehydantoin, Schultzen and Nencki even urea. Taurine likewise, as Salkowski has shown, behaves in a similarly complicated manner. In the human body and in dogs, only uramidoisethionic acid and unaltered taurine are discovered; but in rabbits, taurine when introduced into the intestines is decomposed into thiosulphuric acid, sulphuric acid and urea. The amido acids of the fatty acid series,

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[1] Zeitschrift für physiologische Chemie, **1**, 31.

[2] *Ibid.* **6**, 234.

[3] Archiv f. exp. Patholog. **10**, 268.

[4] *Ibid.* **14**, 379.

[5] Zeitschrift für physiologische Chemie, **2**, 256.

[6] *Ibid.* **6**, 234.

$C_nH_{2n}O_2$, decompose, so far as is known, either wholly or in great part, with formation of urea, only a small portion being excreted unchanged. Salkowski does not agree with Schiffer's[1] belief that the greater part of the sarcosine is excreted unchanged, only about one-fifth being converted into the corresponding uramido acid or anhydride, but considers that the greater part of the sarcosine is excreted in the form of urea; this as a result of experiments on rabbits.[2] From experiments on dogs Salkowski was led to the same conclusion, viz. that glycocoll is in great part changed into urea, a small portion only being excreted unchanged; that sarcosine behaves in a similar manner, the only point of difference being that the portion excreted unchanged is somewhat larger. The formation of urea in the organism, however, is not dependent on the formation of uramido acids, and the uramidobenzoic acid is not formed from the food of the urea.

Chemistry of the Cell Nucleus and its relation to Urea.—It has long been a recognised fact that there is a quantitative relationship, inside the living organism, between phosphoric acid on the one hand and nitrogenous substances on the other. In the vegetable kingdom it has been observed that, in the upbuilding of nitrogenous tissue, there is also an increase of phosphoric acid in the tissue in question. In the animal kingdom, quantitative examinations of the excretory products have led to like results. In the urine of a hungry animal containing a definite quantity of nitrogen there is always found a relative quantity of phosphoric acid. Again, when more nitrogen is taken in the food than appears in the urine, the amount of phosphoric acid found in the excrement is less than that taken in the food, from all of which Kossel[3] infers the possibility of a compound of albuminous matter with certain phosphates or phosphoric acid. As the nearest approach to such a combination we have the nucleins. Their widespread distribution and their relation to the cell nucleus make their metabolism of particular interest. Previous experiments of Kossel[4] have shown that the chemical composition of nuclein is peculiar, and that it is by itself sufficient to explain the above-mentioned appearances. Among its decomposition products is a body which has approximately the composition of albumin, and which furnishes the same decomposition products as the latter, viz. leucine, tyrosine, indol, etc. Such a substance, a compound which, together with phosphoric acid, contains an albuminous-like molecule, has long had an hypothetical existence, as it alone could explain the quantitative relations between the tissue-forming material. The quantitative determination of nuclein presents many difficulties. Kossel, however, has attempted it, estimating not the nuclein itself, but the nuclein-phosphoric acid. Following are a few of the results showing that the quantity of nuclein in the various organs is not inconsiderable.

[1] Zeitschrift für physiologische Chemie, **5**, 266.

[2] *Ibid.* **4**, 107-121, also page 124.

[3] Zur Chemie des Zellkerns. A. Kossel, Zeitschrift f. physiolog. Chem. **7**, 7.

[4] Zeitschrift f. physiolog. Chem. **3**, 284. *Ibid.* **4**, 290.

Percentage of Nuclein-Phosphoric Acid in Moist Tissue.

Spleen from horse,	.867	Brain from sheep,	.313
Spleen " ox,	.636	Muscle " ox,	.092
Liver " dog,	.444	Muscle " ox embryo,	.149
Liver " ox,	.390	Blood, human,	trace
Pancreas " ox,	.580	Blood " in leukaemia,	.286
Kidney " ox,	.285	Pus, "	.154

The proof that the phosphoric acid figures correspond to the content of nuclein in the various organs is to be found in the fact that the organs containing the most cell nuclei (spleen, liver and pancreas) yield much more nuclein-phosphoric acid than the tissue poor in nuclei (blood and muscle). Again, the difference is quite striking in the case of normal blood and leukaemic blood, also in the comparison of developed muscle with the embryonic muscle rich in nuclei.

In addition to the phosphoric acid Kossel likewise determined in several cases the characteristic decomposition products of nuclein, viz. guanine, xanthine and hypoxanthine. It has been suggested that the amount of these latter bodies might be made to serve as an index of the amount of nuclein, but that this view is untenable is manifest from the varying proportion of hypoxanthine found. For while in many of the organs the quantity of hypoxanthine is in proportion to the quantity of nuclein, in the muscles it is not the case. Thus in the muscles of the hen the content of nuclein is extremely small, while the content of hypoxanthine is excessive.

Kossel also calls attention to the fact that there are two so-called nucleins (those from cow's milk and the yolk of egg) which, on decomposition, fail to yield either xanthine, hypoxanthine or guanine, and, in this respect at least, as well as in not coming from cell nuclei, differ from the nuclein present in living tissues. Again, as Kossel points out, his quantitative results show plainly that those organs to which we ascribe special activity, as in the nutritive and regenerative processes of the animal body, liver and spleen for example, contain far more phosphoric acid in the form of nuclein than the locomotor apparatus. A study was likewise made of the proportion of nuclein in the liver and muscle of hens at different stages of digestion, and at the same time xanthine and hypoxanthine were determined together with total nitrogen and solids. Following are the results in percentage of the moist tissue.

	Liver.		Breast muscle.	
	Hungry.	Fed.	Hungry.	Fed.
Nuclein-phosphoric acid	.511	.264	.150	.111
Solids	29.500	39.500	27.400	27.000
Nitrogen	4.250	4.410	4.450	4.410
Xanthine	...	...	.038	.011
Hypoxanthine	...	...	.073	.129

As is seen from the table, the content of nuclein-phosphoric acid is not noticeably different in the muscle under the different conditions, while in the liver a decided difference is noticed. From this it is apparent that the nuclein-phosphoric acid during the condition of hunger is less readily withdrawn from the tissue than the remaining phosphoric acid compounds. Plainly the results afford no evidence whether in the tissue of such organisms as are forced to live upon their own tissue, a decomposition of nuclein takes place. In the attempt to settle this point Kossel made several experiments, which led him to the belief that nuclein cannot be considered as a "reserve fund" upon which the organism can live, for, as he remarks, the quantity of nuclein varies but little either in hunger or in full digestion. The physiological function of the nuclein is rather to be sought for in relation to the formation of new cells in the upbuilding of the tissue. A comparison of the nuclein content of a rapidly developing embryonal muscle, with that of a fully developed one, lends favor to this view.

While from previous experiments Kossel had found that both xanthine and hypoxanthine were formed from nuclein, guanine, which by the action of nitric acid is changed into xanthine, has likewise been proved to be a decomposition product of nuclein. In this connection it is well to remember that guanine through oxidation yields guanidine, and this in turn urea; thus by bringing these bodies into genetical relationship we have a series, the two end members of which are on the one hand urea, on the other the cell nucleus. The production of urea from guanine in the organism has, as Kossel remarks, been plainly demonstrated by the feeding experiments of Kerners.[1] Again, in support of a possible production of uric acid from hypoxanthine, we have the fact that the muscles of such organisms as excrete uric acid as the chief product of their metabolism are much richer in hypoxanthine than those of man or the horse. As another support to this view there is the fact that in leukaemia, where the nitrogenous bases of blood, guanine, xanthine and hypoxanthine, are greatly increased, which Kossel deems due to the increased number of cell nuclei, the quantity of uric acid excreted is likewise greater.

Kossel has repeated Demant's[2] experiments regarding the behavior of these three nitrogenous bases under the various physiological conditions of the body, and has found, contrary to Demant's results, only a slight diminution of hypoxanthine in the hungry condition, as is seen from the foregoing table. From an examination of the liver, spleen and blood in a case of leukaemia, Kossel found that the amount of hypoxanthine in the two former organs was not essentially different from the amount normally present, while in the blood the amount was greatly in excess of the normal quantity. Accepting the view that the cell nucleus is the mother-substance of hypoxanthine, we should naturally expect a change in the percentage amount of hypoxanthine in those places where the white nucleated blood corpuscles appear in the place of the red corpuscles; but little or no change in those organs where, in consequence of the leukaemic disease, nucleated cells of the normal organ are displaced by nucleated cells of pathological origin. Hence the above percentages of hypoxanthine in leukaemia are such as would be expected in view of the origin of the base in nuclein.

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[1] Annalen der Chemie, **103**, 249.

[2] Zeitschrift für physiologische Chemie, **3**, 381.

R. H. CHITTENDEN.

ON THE DIFFERENT MODIFICATIONS OF SILVER BROMIDE AND SILVER CHLORIDE.

Hermann W. Vogel has made a comparative study of the properties of silver bromide, obtained by precipitation in an aqueous solution of gelatin, and those of the same compound prepared by precipitation in an alcoholic solution of collodion. In 1874 Stas called attention to six modifications of silver bromide. One of these, granular bromide of silver, obtained by boiling the flocculent precipitate for several days with water, he stated was the most sensitive to light of all substances known; exposure for two or three seconds to the pale blue flame of a Bunsen burner being sufficient to blacken it. Important as this fact was for photographers it was not applied for years, and it was only in 1878 when, it having been found that silver bromide precipitated in a gelatin solution and boiled for several hours becomes much more sensitive to light, that the remarks of Stas were recalled. To-day these observations have become of the greatest importance to practical photography. They have led to the preparation of the silver bromide gelatin emulsion and the silver bromide gelatin plates, which are twenty times more sensitive than the silver iodide collodion plates, and have become indispensable when impressions are to be taken in a dim light.

The extraordinary sensitiveness of silver bromide in gelatin seemed the more remarkable since it was known that silver bromide in collodion is only moderately sensitive. The explanation was sought for in various directions, but as the result of numerous investigations it appears that the chief cause of the difference is the presence of different modifications of silver bromide. From a consideration of the work already done on the subject, Vogel suspected that silver bromide precipitated in an aqueous colloidal liquid would have notably different properties from silver bromide precipitated in an alcoholic colloidal solution. Silver bromide was prepared in many different ways. Emulsions were made in bromide solutions containing gelatin or collodion (the former aqueous, the latter alcoholic), some with the aid of heat, others without. Part of the emulsion was then poured upon plates kept at a moderate temperature and dried. The remainder was boiled or treated with ammonia before being applied to the plates. He also precipitated silver bromide in dilute gelatin or collodion solutions, allowed it to settle completely, washed the precipitate, and mixed it with a new portion of gelatin or collodion before applying it to the plates. Finally he precipitated pure silver bromide, in the absence of all colloids, by means of pure aqueous or alcoholic solutions of bromides and attempted to bring this upon plates, using gelatin or collodion as a cement. The result of all these experiments is that there are essentially two modifications of silver bromide, the one being obtained by precipitation in aqueous, the other in alcoholic solutions. The first, on account of the position of the maximum of sensitiveness for the solar spectrum, he calls blue sensitive, the other for the same reason indigo sensitive.

It is of no consequence whether the aqueous or alcoholic solution in which the silver bromide is formed contains gelatin or collodion, or whether the precipitation is effected with excess of bromide or of silver nitrate. It makes no difference whether the solution is hot or cold, or whether the silver bromide is treated with ammonia or whether it is boiled or not. The only necessary condition is that in precipitating indigo sensitive silver bromide the solutions must contain at least 96 per cent. of alcohol. From aqueous alcoholic solutions blue sensitive silver bromide is precipitated.

Besides the difference of sensitiveness towards the solar spectrum, these modifications of silver bromide exhibit other characteristic differences in properties which indicate beyond a doubt that they are two essentially different modifications of the same substance. Among these are, 1st. Their unequal divisibility in gelatin or collodion solutions. The indigo sensitive silver bromide cannot be distributed through a gelatin solution, while the blue sensitive modification does so very readily. 2d. Their unequal reducibility ; the blue sensitive silver bromide being reduced with much greater difficulty than the indigo sensitive variety. 3d. Their different action toward chemical and physical sensitizers. 4th. Their different action toward photographic developers. 5th. Their different action under the influence of heat. The blue sensitive variety if heated under water has its sensitiveness perceptibly increased, while the other is not changed by such treatment.

A direct transformation of one modification into the other has not yet been accomplished. The effect of the light upon these substances is incipient reduction, and we might hence suppose that the more easily reducible indigo sensitive variety would be the more sensitive to light. But this is not the case, because it is not chemical reducibility, but the absorption power for light that is of the greatest importance. Now the blue sensitive silver bromide has a greater absorption power than the indigo sensitive variety, and hence its greater sensitiveness. Silver chloride prepared by methods similar to those used in making the two forms of bromides was also found to exist in two modifications. One is designated as ultra violet sensitive, the other as violet sensitive silver chloride.—(*Berichte der deutschen chemischen Gesellschaft*, **16**, 1170.) E. H. K.

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ON PROPIMINE SULPHOCYANIDE.

BY J. TSCHERNIAC AND T. H. NORTON.

If monochlor-acetone be exposed to the action of ammonium sulphocyanide in alcoholic solution, the sulphocyanide of a new base is formed according to the following reaction:

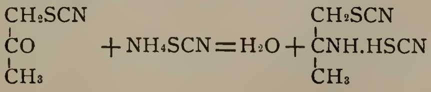
$$2NH_4SCN + C_3H_5OCl = NH_4Cl + H_2O + C_4H_6N_2S.HSCN.$$

This reaction takes place even when the monochlor-acetone is in large excess.

Later experiments showed us that this new compound is the result of two successive reactions. In the first of these,

$$NH_4SCN + C_3H_5ClO = NH_4Cl + C_3H_5OSCN,$$

acetone sulphocyanide is formed. In the second reaction this latter compound is decomposed by ammonium sulphocyanide, the formation of the sulphocyanide $C_4H_6N_2S.HSCN$ being accompanied by the separation of a molecule of water:



$$\begin{array}{l} CH_2SCN \\ | \\ CO \\ | \\ CH_3 \end{array} + NH_4SCN = H_2O + \begin{array}{l} CH_2SCN \\ | \\ CNH.HSCN \\ | \\ CH_3 \end{array}$$

We have given the name of propimine sulphocyanide to the base $C_4H_6N_2S$, as expressing most exactly its composition.

Preparation of the Sulphocyanide of the new base.—Two parts of ammonium sulphocyanide are dissolved in six parts of warm 90 per cent. alcohol; one part of monochlor-acetone is then added to the solution, which is allowed to stand for 24 hours. The precipitated ammonium chloride is then removed by filtration and washed with absolute alcohol. The filtrate and the alcohol used in washing are next evaporated on the water-bath, and the residue is dissolved in four times its weight of cold water. After standing for several days, a thick, viscous precipitate separates from the deep red solution, which is carefully decanted. The solution thus obtained is decolorised by boiling several times with animal charcoal, and is then concentrated to 110°. On cooling, the sulphocyanide of the new base is deposited in the form of thick crystalline crusts, while the ammonium salts which are present remain in the residual liquors. The sulphocyanide is obtained in a state of purity by renewed treatment with animal charcoal and recrystallisation. This method of preparation furnishes one-third of the theoretical yield.

The analysis resulted as follows:

(1) 0.3955 gram gave 0.149 gram H_2O, and 0.510 gram CO_2.

(2) 0.2365 gram gave 0.0571 gram N by Will and Varrentrap's method.

(3) 0.2305 gram gave 0.0552 gram N by Dumas' method.

(4) 0.202 gram gave 0.5393 gram $BaSO_4$ by Carius' method.

(5) The sulphocyanic acid was titrated by Volhard's method, and the precipitated silver sulphocyanide was weighed.

	Calculated.	Found.				
		(1)	(2)	(3)	(4)	(5)
C_5	34.68	35.17	...	...	...	...
H_7	4.04	4.12	...	...	...	...
N_3	25.28	...	24.14	23.95	...	...
S_2	37.0	...	...	...	36.63	...
HSCN	34.1	...	...	...	...	34.0 34.2 34.45

This salt is obtained in the form of large, handsome crystals, usually of a light yellow color, but almost colorless when in a state of great purity. It melts at 114°–115°, becomes red at 175°, and is decomposed above this temperature. It is very soluble in alcohol and hot water, from the latter of which it is easily crystallised. The aqueous solution gives all the ordinary reactions of soluble sulphocyanides. The free base is obtained in the form of colorless drops when potash is added to the strongly concentrated solution.

Nitrate of Propimine sulphocyanide, $C_4H_6N_2S.HNO_3$, results from the double decomposition of the salt just described with silver nitrate, or from the neutralisation of the free base with nitric acid. It crystallises in the form of colorless needles from its aqueous solution, melts at 183°, and is decomposed with detonation above 200°.

0.325 gram gave 0.1265 gram H_2O and 0.321 gram CO_2.

Calculated for $C_4H_6N_2S.HNO_3$.		Found.
C	27.12	26.94
H	3.95	4.30

Sulphate of Propimine sulphocyanide, $C_4H_6N_2S.H_2SO_4.2H_2O$, is obtained in a similar manner. It crystallises from the aqueous solution in the form of small white needles.

Calculated.		Found.
H_2SO_4	39.51	40.09

Chloroplatinate of Propimine sulphocyanide, $(C_4H_6N_2S.HCl)_2PtCl_2$, is obtained in the form of a brownish yellow powder when platinum chloride is added to the solution of the base in hydrochloric acid.

0.301 gram gave 0.092 gram Pt.

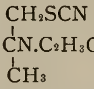
Calculated.		Found.
Pt	30.80	30.66

Preparation of the free base.—A concentrated solution of caustic potash is added in slight excess to pure crystals of the sulphocyanide described above. The liberated base is extracted by means of ether; the ethereal solution is dried over potash; and after driving off the ether on the water-bath, the base is obtained in a state of purity by distillation in a vacuum on an oil-bath.

The base is thus obtained in the form of a colorless, crystalline mass melting at 42°. This compound exhibits in a striking manner the phenomenon of surfusion. When once melted, congelation does not ensue until the temperature has fallen to 28°. As soon as the congelation has commenced, the temperature mounts to 42°, and remains unchanged up to the end of the solidification. It distills at 136° without decomposition under a pressure of 3–4 cm. of mercury. Under ordinary atmospheric pressure it distills at 231°–232°, but undergoes a slight decomposition. It is exceedingly hygroscopic, and very soluble in water, alcohol and ether. The aqueous solution possesses an alkaline reaction. When preserved in bottles which are not hermetically closed, it slowly blackens, and finally gives rise to products of a resinous nature.

0.374 gram gave 0.753 gram $BaSO_4$.

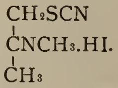
	Calculated.	Found.
S	28.07	27.64



Acetyl-propimine sulphocyanide, $\begin{matrix}CH_2SCN\\ |\\ CN.C_2H_3O\\ |\\ CH_3\end{matrix}$. This compound is obtained by mixing equal weights of the free base and of acetic anhydride. The reaction is accompanied by a notable evolution of heat, and is completed by warming on the water-bath. After adding water and neutralising with potassium carbonate, the acetyl compound separates in the form of hard white crusts. These are rubbed together with a small amount of water in a mortar, and the water is drawn off by means of a vacuum pump. The compound is obtained in a state of purity by dissolving in ten times its weight of boiling water, allowing to crystallise, and drying the crystals over sulphuric acid. The yield is nearly theoretical. The white, fine silky crystals prepared in this manner possess a brilliant diamond lustre. They melt at 134°, and solidify at 91°. They are but slightly soluble in cold water; the solubility is, however, notably increased by the addition of acids or caustic alkalies.

0.274 gram gave 0.462 gram CO_2 and 0.135 gram H_2O.

	Calculated.	Found.
C	46.15	45.98
H	5.13	5.47



Hydroiodide of Methyl-propimine sulphocyanide, $\begin{matrix}CH_2SCN\\ |\\ CNCH_3.HI.\\ |\\ CH_3\end{matrix}$

Equal molecular weights of methyliodide and propimine sulphocyanide are brought together. The reaction, which is extremely violent at first, is completed by heating for several hours on a water-bath. The yield is theoretical. By crystallisation in water the product is easily purified. It is thus obtained in the form of brown, transparent scales. It melts at 159.5° ; is soluble in two parts of hot water and ten parts of cold water.

0.383 gram gave 0.323 gram CO_2 and 0.1475 gram H_2O.

0.242 gram gave 0.215 gram AgI.

	Calculated.	Found.
C	23.44	22.97
H	3.52	4.25
I	49.60	49.42

The free methyl-propimine sulphocyanide cannot be distilled without decomposition.

Laboratory Notes from the University of Cincinnati.

XXVII.—ON SOME PHOSPHIDES OF IRIDIUM AND PLATINUM.

By F. W. Clarke and O. T. Joslin.

In May, 1881, Mr. John Holland, a manufacturer of gold pens in Cincinnati, took out a patent for a process of fusing iridosmine. For pointing gold pens, only selected grains of the native mineral were suitable; and his object was to utilise the quantities of unavailable mineral which accumulated in his establishment. His process, briefly stated, consisted in heating the ore to whiteness, and then throwing in upon it common phosphorus; fusion at once took place, and the excess of phosphorus was afterwards removed by heating the product in contact with lime. The metal thus produced was harder than steel, brilliantly lustrous, insoluble in acids, and available for a great variety of purposes. As the process has already been fully described by Professor W. L. Dudley,[1] it needs no further technical discussion here. Our work relates to the chemical side of the new iridium industry.

At an early date, samples of the "fused iridium" were placed in our hands for examination, together with some of the original ore from which the melts had been made. The latter was a Californian iridosmine, in hard, brilliant grains, of specific gravity 19.182. Of the fused product the sp. gr. was only 13.768.

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[1] Sci. Proc. Ohio Mechanics Institute, Jan. 1882.

Two portions of the latter were prepared at different times, for comparison with the native mineral, and partial analyses were made. In the first portion, phosphorus only was determined, three estimations giving respectively 7.52, 7.58, and 7.74 per cent. This portion contained barely a trace of osmium.

In the iridosmine itself 15.38 per cent. of osmium were found; and accordingly the second fused portion was examined with special reference to this element. As far as it was carried out, the analysis gave the following results:

Iridium,	80.82
Osmium,	6.95
Phosphorus,	7.09
Ruthenium and Rhodium,	7.20
	102.06

No attempt was made to separate the ruthenium and rhodium, nor to trace out the cause of the plus error. The phosphorus agrees reasonably well with the estimations made in the first portion; and the low percentage for osmium, compared with the mere trace in the other lot and the large amount in the ore, shows that this element is more or less eliminated according to the circumstances attending fusion. The "fused iridium" is plainly, as might be expected, a phosphide; and the percentage of phosphorus indicates a compound having the formula Ir_2P. For this formula the percentage of phosphorus should be 7.43, and evidence in its favor will appear farther on. Of course the product is far from pure, containing the phosphides of the other metals of the group; but its general nature is evident. With pure iridium as the starting point, a pure Ir_2P would probably be obtained.

Since it seemed desirable to ascertain how platinum would behave when treated like the iridium, experiments in that direction were undertaken. The metal used was a worn-out platinum crucible, carefully cleaned, of which a sample was first analysed. The results were as follows:

Platinum,	97.22
Iridium,	2.49
Copper,	.46
Palladium,	a trace
	100.17

15.4200 grams of this material were heated to whiteness in a hessian crucible, and 20 grams of stick phosphorus were thrown in. Fusion at once took place, and when the excess of phosphorus had burned off, the mass was allowed to cool. We thus obtained a brilliant, silver white, brittle button, weighing 19.4663 grams. As it was porous, we did not determine its specific gravity. If we reckon the iridium in the mass as platinum, and ignore the trifling amount of copper, the increase in weight gives us synthetically the following composition for the product:

	Found.	Calculated for Pt_3P_5.
Platinum,	79.21	79 05
Phosphorus,	20.79	20.95
	100.00	100.00

These figures are useful only in confirmation of our subsequent analyses.

A portion of the phosphide, coarsely powdered, was next boiled for at least forty hours with aqua regia. At the end of that time a considerable portion was still undissolved, and trial showed it to be quite insoluble in the reagent. The soluble portion amounted to 71.21 per cent. of the whole, and the insoluble part to 28.79 per cent. The latter, dissolved by fusion with sodium nitrate and caustic soda and subsequent boiling with aqua regia, was analysed separately, and proved to be a definite phosphide of the formula PtP.

	Found.	Calculated for PtP.
Platinum,	86.16	86.28
Phosphorus,	14.03	13.72
	100.19	100.00

The soluble fraction, also analysed independently, agreed approximately with the formula PtP_2.

	Found.	Calculated for PtP_2.
Platinum,	76.62	75.88
Phosphorus,	23.68	24.12
	100.30	100.00

Recalculating the analyses of the two fractions so as to express the composition of the original phosphide, we get the following results to compare with those obtained by synthesis.

	Found, analysis.	Found, synthesis.	Calculated for Pt_3P_5.
Pt,	79.39	79.21	79.05
P,	20.87	20.79	20.95
	100.26	100.00	100.00

The data for the foregoing calculations, in weights, are as follows: Weight of sample, 2.2042 grams. Dissolved, 1.5695 gram; undissolved, .6347 gram. Platinum in the soluble portion, 1.2025 gram; in the insoluble, .5475 gram; total, 1.7500 gram. Phosphorus in the soluble portion (calculated from weight of $Mg_2P_2O_7$), .3717 gram; in the insoluble, .0891 gram; total, .4608 gram. These figures further show that the ratio between the dissolved and insoluble phosphides agrees well with the equation $Pt_3P_5 = PtP + 2PtP_2$.

	Found.	Calculated.
Insoluble PtP,	28.79	30.54
Soluble PtP_2,	71.21	69.46
	100.00	100.00

The slight discordance here, 1.75 per cent., taken together with the fact that the platinum in the soluble part came out rather too high, shows that a trifling quantity of the PtP was dissolved by the very prolonged action of the aqua regia to which it had been subjected. In other words, the fractionation of the Pt_3P_5 into the two simpler phosphides is not quite perfect.

In order to determine whether the complex phosphide Pt_3P_5 could be reduced to metal by long heating, two portions were roasted in a muffle until constant weight was obtained. The losses in weight were 14.08 and 13.78 per cent. respectively. The product of this roasting was malleable, and readily soluble in aqua regia. It contained 7.36 per cent. of phosphorus, which is just the amount required by the formula Pt_2P. Here then we have a fourth phosphide analogous in composition to the fused iridium, and confirmatory of the formula assigned to the latter. The reduction of Pt_3P_5 to Pt_2P should require a loss of 14.66 per cent. In all of these calculations we have taken 195 for the atomic weight of platinum. The trace of copper in the original platinum did not show itself in any of the analyses of the phosphides, and the small amount of iridium present could nowhere affect our results by more than a hundredth of a per cent.

In conclusion, our experiments show the existence of three simple phosphides of platinum, PtP_2, PtP, and Pt_2P, and of a double phosphide Pt_3P_5. Of these compounds the monophosphide, by virtue of its insolubility in aqua regia, is the most noteworthy. The compound PtP_2 is probably identical with the phosphide described by Schrötter,[1] who obtained it, as well as analogous phosphides of iridium and palladium, by heating the finely divided metal in phosphorus vapor. As far as we can learn, no other platinic phosphides have ever been regularly analysed. Pelletier[2] heated platinum with phosphorus and found that 300 grains of the former took up 54 of the latter; results which approximate roughly to the ratio PtP. Edmund Davy[3] tried two sets of experiments in the same direction. First, he heated ammonium chloroplatinate with phosphorus, and obtained a black compound of doubtful composition. Afterwards he heated platinum and phosphorus together in a vacuum, and obtained results which, calculated synthetically, agree well with the formula Pt_3P_4. This product was insoluble in strong acids, and at the time (1812) could not be directly analysed.

XXVIII.—ON CADMIUM IODIDE.

By F. W. Clarke and E. A. Kebler.

Of late years the suggestion has repeatedly been made, by various chemists, that the definite series of related chemical elements may be analogous in character to series of compounds such as the hydrocarbons. For example, fluorine, chlorine, bromine, and iodine form one such series; the nitrogen group, from nitrogen to bismuth, forms another, etc. There have been many efforts to trace relationships between the atomic weights in these and other similar series, and so to get evidence in favor of the foregoing hypothesis; but except in the establishment of the periodic law, all such attempts seem to have ended fruitlessly.

But notwithstanding the failure to discover definite numerical relations between the elements, the evolutionary speculation is suggestive. If the series of elements are developed progressively, like series of compounds, there should be various points of comparison; and one line of thought is as follows. In any series of compounds, the possibility of isomerism increases as we ascend; and therefore, by analogy, we should expect to find a similar state of affairs among the so-called elements. The derivatives of the highest member of a series should be more numerous and complex than those of lower members, and cases of allotropy or isomerism ought also to be more frequent. Whether this is so or not in all known instances we do not attempt to say; our experiments bear upon a single point, and that may be stated briefly.

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[1] Sitzungsberichte Wien Akad. 1849, 301.

[2] Ann. de Chimie, **13**, 1792, 101–143.

[3] Tilloch's Mag. **40**, 1812, 27–39. Schweigg. Journ. **10**, 382.

It is a well-known fact that allotropy is common among the metallic iodides, and much more so than among the corresponding compounds of chlorine and bromine. For example, the scarlet and yellow modifications of mercuric iodide, and the three varieties of antimony iodide may be cited. We have been engaged in the study of several other iodides, especially that of cadmium, and in this case we are now prepared to announce the existence of two distinct modifications. So far then our results lend countenance to the speculative idea which we began by quoting, even though much weightier evidence would be needed to put it upon the basis of a clear and definite theory. The speculation, however, instigated our experiments, and in their success its utility as a means of stimulating research is justified.

Up to the present time but two determinations of the specific gravity of cadmium iodide have been published. First, by Bödeker, who found it to be 4.576 at 10°; and second, by Fullerton, whose mean result was 5.9798. The latter determination was made some years ago in this laboratory, and is undoubtedly too high; but the discordance between the two is so great that it could hardly be ascribed to error. Accordingly, we prepared cadmium iodide by a variety of methods, and obtained the following determinations of specific gravity. All weighings were made in benzene, and the results are referred to water at 4° as unity. Our mean figures may be stated first, and the details given later.

A. Cadmium and iodine, in equivalent quantities, were heated together in a sealed tube from which the air had been exhausted. The product was white, and contained 1.30 per cent. of residue insoluble in water. Its character was established by analysis, and we found it to contain about 98.5 per cent. true CdI_2. Sp. g. 5.543.

B. Cadmium and iodine were digested together under water.

The crystals obtained by evaporation were carefully identified as CdI_2. Sp. g. 5.622.

C. A very fine sample of iodide prepared by Schuchardt, of Goerlitz, was examined. Its mode of preparation, as stated in a letter from the maker, consisted in dissolving together equivalent quantities of cadmium sulphate and potassium iodide, evaporating to dryness, extracting with alcohol and crystallising. Sp. g. 5.660.

D. Preparations A and B were mixed and recrystallised from alcohol. The sp. g., as determined by Mr. E. Twitchell, was 5.701.

So far at least the variations in our results were not startling. Our next series came out differently.

E. Cadmium carbonate was dissolved in hydriodic acid. The solution, discolored by free iodine, was rendered nearly colorless by cadmium clippings, and crystallised. Sp. g. 4.612. A second series of determinations gave 4.596. Both figures agree well with Bödeker. The salt was analysed, with results as follows:

	Found.	Calculated for CdI_2.
Cadmium,	30.40	30.60
Iodine,	69.33	69.40
	99.73	100.00

F. To verify these results, if possible, another lot of iodide was prepared with carbonate and acid, but the solution was not decolorised by metal. Sp. g. 5.729. The sample on analysis yielded 30.56 per cent. of cadmium.

G. Another solution was prepared as under F, and divided into two parts. One was allowed to evaporate spontaneously at a low temperature. Sp. g. of product 5.610.

H. The second part of solution G was boiled down rapidly. Sp. g. of iodide 5.675.

I. Metallic cadmium was dissolved in hydriodic acid, The solution yielded a pure iodide of sp. g. 4.688, as determined by Mr. Twitchell. This preparation dried at 50°, became silver grey and its sp. g. rose to 5.141. Again heated to 50° the sp. g. rose to 5.536. A third heating brought it up to 5.545. Accompanying this change there was a little decomposition which resulted in the formation of a trifling amount of insoluble material.

The foregoing results all point pretty definitely to the existence of two allotropic varieties of cadmium iodide, differing in specific gravity by about a unit. The higher density represents a union of cadmium and iodine with little or no change of volume, while the lower corresponds to a noteworthy expansion and consequent instability. The higher or normal salt, which we may call α cadmium iodide, is white, and undergoes no perceptible change when heated to any temperature below 250°. The lower or β salt is brownish, and loses weight even at 40°. One sample lost 5.50 per cent. at 50°, an alteration which is undoubtedly due to the formation of an oxide or oxyiodide with liberation of iodine. The increase in specific gravity upon heating may be partly due to the same change, but is mainly ascribable to a transformation of the β into the α modification. The conditions governing the formation of the new salt are obscure and need farther study. In our experiments we obtained it only twice, and in each case cadmium was acted upon by hydriodic acid. In the first instance, however, this action was only incidental to the decolorisation of a solution of iodide otherwise prepared, and was necessarily very trifling. In both cases, however, cadmium iodide was exposed to the action of nascent hydrogen, and it is probable that the latter had something to do with the production of the β compound. This suggestion we offer merely as a clue for use in further study, without any speculations as to just how the reactions proceeded.

In detail, our specific gravity determinations were as follows, including the temperatures of weighing. The series are lettered as before:

I. *The normal* CdI_2.

A.	B.	C.	D.
5.539, 20.4°	5.622, 15.2°	5.697, 17.5°	5.716, 14.8°
5.530, 20.1	5.618, 15.2	5.704, 18.	5.714, 15.3
5.530, 20.1	5.638, 15.2	5.630, 18.2	5.696, 15.5
5.574, 20.2	5.629, 15.4	5.650, 18.1	5.696, 15.8
5.543, 19.9	5.630, 15.6	5.642, 18.2	5.685, 15.9
5.543, 19.9	5.621, 16.1	5.626, 18.2	
5.523, 19.8	5.610, 16.6	5.672, 18.2	
5.564, 20.1	5.611, 16.6		
5.543	5.622	5.660	5.701

F.	G.	H.
5.750, 10.5°	5.580, 17.6°	5.682, 15.0°
5.740, 10.5	5.610, 17.4	5.654, 15.2
5.715, 10.6	5.660, 17.7	5.683, 15.1
5.747, 10.5		5.682, 15.0
5.719, 10.6		
5.705, 10.6		
5.729	5.610	5.675

Total, 41 weighings. Mean of all, 5.644.

II. β CdI_2.

E_1.	E_2.	I.
4.618, 14.0°	4.598, 15.2°	4.697, 18.8°
4.607, 14.4	4.594, 15.3	4.713, 18.9
4.609, 14.7	4.601, 15.2	4.740, 19.0
4.618, 15.0	4.602, 15.2	4.668, 19.0
4.612, 15.1	4.592, 15.4	4.625, 18.9
4.615, 15.1	4.593, 15.4	
4.605, 15.2	4.595, 15.2	
4.612	4.596	4.688

Total, 19 weighings. Mean of all, 4.626.

Molecular volume, α salt, 64.8
" " β " 79.2

Mol. vol. $Cd + I_2$, 64.3, when sp. g. iodine $=$ 4.948 (Gay Lussac), and sp. g. Cd $=$ 8.655 (Matthiessen).

In connection with these experiments a little work was done upon the double iodides of cadmium. Attempts were made to prepare such double salts with the iodides of lead and of thallium, but unsuccessfully. Mercuric iodide dissolved freely in a hot solution of cadmium iodide, and the liquid, upon cooling, deposited scarlet crystals of the first-named salt unaltered. The mother liquor from these crystals, upon longer standing, yielded golden laminae, which were recrystallisable from hot alcohol. They were anhydrous, and contained iodine, cadmium and mercury. A partial analysis pointed to the formula $CdI_2.3HgI_2$.

	Found.		Calculated.
Cadmium,	6.90		6.48
Iodine,	58.80		58.98
Mercury,	34.30	by difference.	34.54
	100.00		100.00

There was not enough of this salt to admit of further investigation.

With other iodides we have not yet gone very far. Zinc iodide, prepared by direct union of the elements and sublimation in a stream of carbon dioxide, has a sp. gr. of 4.666.[1] Bödeker found a sp. gr. of 4.696. For a somewhat impure bismuth iodide from Schuchardt we found the sp. gr. to be 5.548. Bödeker's value was 5.652.

With stannic iodide we are still engaged. Suffice it to say that we are satisfied of the existence of at least two modifications, one darker red and less soluble in benzene than the other. But the difficulty of obtaining pure and definite products is very great, and we may not have time to complete the investigation.

XXIX.—SOME SPECIFIC GRAVITY DETERMINATIONS

By F. W. Clarke.

The following specific gravity determinations were made under my supervision by the students named below. The salts were weighed in benzene, and the density of water at 4° was taken as unity. Each figure is the mean of several closely concordant results.

Uranyl sulphate, $(UO_2)SO_4.3H_2O$, 3.280 at 16.5°. H. Schmidt.

Uranyl ammonium sulphate, $(UO_2)Am_2(SO_4)_2.2H_2O$, 3.0131 at 21.5°. H. Schmidt.

Uranyl potassium sulphate, $(UO_2)K_2(SO_4)_2.2H_2O$, 3.363 at 19.1°. H. Schmidt.

Double salt, $K_2CrO_4.2Hg(CN)_2$, 3.564 at 21.8°. H. Schmidt.

Ferric chloride, sublimed, Fe_2Cl_6, 2.804 at 10.8°. J. P. Grabfield.

Ferrous " $FeCl_2$, 2.988 at 17.9°. J. P. Grabfield.

Chromic " violet, Cr_2Cl_6, 2.757 at 15°. J. P. Grabfield.

Chromous" $CrCl_2$, 2.751 at 14°. J. P. Grabfield.

The last compound contained 14 per cent. of chromic oxide as an impurity, and the sp. gr. actually found was 3.067. This, corrected by means of Schröder's value for Cr_2O_3, 5.01, gives the sp. gr. assigned above.

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[1] Value actually found, 4.736. This was corrected for 3.13 per cent. of admixed metal, becoming 4.666. There were six concordant estimations.

Strontium chloride, cryst., $SrCl_2.6H_2O$, 1.964, 16.7°. E. Muehlberg.
Cadmium chloride, $CdCl_2$, 3.655, 16.9°. P. A. Knight.
" bromide, $CdBr_2$, 4.794, 19.9°. "
" fluoride, CdF_2, 5.994, 22.0°. E. A. Kebler.
Thallium iodide, precipitated, TlI, 7.072, 15.5°. E. Twitchell.
" " after fusion, TlI, 7.0975, 14.7°. E. Twitchell.
" bromide, precipitated, TlBr, 7.540, 21.7°. H. Keck.
" " after fusion, " 7.557, 17.3°. "
Lead bromide, precipitated, $PbBr_2$, 6.572, 19.2°. "
Silver tartrantimonite, $SbAgC_4H_4O_7$, 3.4805, 18.2°. C. S. Evans.

XXX.—RESEARCHES ON THE TARTRATES OF ANTIMONY.

By F. W. Clarke and Charles Seth Evans.

Although some of the double tartrates of antimony, such as the tartar emetics, have been quite elaborately studied, our knowledge of its simple tartrates has hitherto been singularly inexact and vague. According to Bergmann,[1] a solution of antimonious oxide in aqueous tartaric acid crystallises confusedly; while according to Dulk[1] it does not crystallise at all. Berzelius[2] and Peligot[3] both obtained large crystals, but assigned different formulæ; Berzelius without analysis, Peligot after investigation. Peligot, however, must have calculated his formula upon the basis of Sb=129, the old Berzelian determination; and his analysis, recalculated with the modern value of Sb=120, leads to no intelligible symbol. The precipitate formed by alcohol in solutions of the crystalline tartrate was also examined by Berzelius and by Peligot; and here again, upon incomplete analyses, different formulæ were based. In short, neither Berzelius nor Peligot studied these compounds at all thoroughly; and the subject, up to the time when we began our own experiments, was in a most confused state. Inferences were more numerous than facts, and the latter needed scrupulous reverification. We believe that we have succeeded in shedding some light upon the nature of the substances in question; and that the results which we have obtained may form a fair basis upon which to conduct future investigations.

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[1] See Gmelin's Handbook, edition of the Cavendish Society, **10**, 297.

[2] Lehrbuch, 5 Aufl. **3**, 1124.

[3] Annales de Chim. et de Phys. 3 série, **20**, 289.

Antimony trioxide, as is well known, is readily soluble in aqueous tartaric acid; but the properties of the solution depend upon the relative proportions of its constituents. When the oxide is dissolved in the acid to complete saturation, the solution yields no crystals whatever; but upon evaporation dries up to a gummy, amorphous mass. With less oxide and an excess of acid, crystallisation becomes possible, and in every case of this kind, rosettes of needles are obtained. If the acid is in slight excess, crystallisation takes place with difficulty, and the smaller the proportion of the oxide the more easily the crystals form. In all cases, however, in which the crystallisation occurs, the mother liquors are exceedingly viscous and consequently difficult to remove; so that it is by no means easy to secure pure products for examination. Furthermore, the crystals vary in composition, as the following percentages of antimony will show:

1. 40 grams of Sb_2O_3 were boiled with 60 grams of tartaric acid. The solution was incomplete. The filtered liquid, evaporated to dryness, gave a product containing 27.53 per cent. of antimony.

2. 35 grams Sb_2O_3 to 60 of acid. Yielded indistinct crystals which could not be purified for analysis.

3. 30 grams Sb_2O_3 to 60 of acid. Crystals washed and twice recrystallised. Per cent. of Sb, 18.92.

4. 20 grams Sb_2O_3 to 60 of acid. Product recrystallised. Several distinct lots of material gave crystals containing antimony in the following percentages:

A	13.35		
B	15.90		
C	16.48	16.64	
D	16.18	16.21	17.16
E	17.88	18.00	

The last product was dried with extreme care and examined further. The results will be given later.

5. 15 grams Sb_2O_3 to 60 of acid. Product recrystallised. Per cent. of Sb, 5.37. Probably a mixture.

6. 12 grams Sb_2O_3 to 60 of acid. Per cent. of antimony in crystals, 3.69 to 3.82. Probably a mixture.

The antimony was weighed as sulphide in every case, and the results indicate two things: First, the difficulty of obtaining definite products; and second, the probable existence of a series of salts. Two of the latter were analysed, as follows:

First. The crystals marked 3 and the preparation 4 E. of the foregoing table had all the characteristics of definite compounds. They proved to be identical, and to be closely represented by the formula $Sb(C_4H_4O_6)_3H_3.4H_2O$.

	Found.				Calculated.
	3.		4 E.		
Sb	18.92	17.88		18.00	18.78
C	22.59	22.98		23.19	22.53
H	3.78	3.39		3.78	3.60
Water at 120°	11.05		10.98		11.27

In brief, this tartrate, which may fairly be called antimonio-tritartaric acid, is simply a triple molecule of tartaric acid with half its replaceable hydrogen replaced by an atom of trivalent antimony. It crystallises in rosettes of white needles and is easily soluble in water. With carbonates it effervesces strongly and behaves like a weak acid. Its reactions in this particular will be considered further on. With alcohol its solution yields a copious white precipitate, which, washed with alcohol and thoroughly dried over sulphuric acid, proved to be neutral antimonious tartrate, $Sb_2(C_4H_4O_6)_3.6H_2O$.

	Found.		Calculated.
Sb	30.58	30.76	30.30
C	18.14		18.18
H	3.01		3.03
Water at 160°	13.86		13.63

This salt is easily soluble in water. In its cold solution sodium carbonate produces no turbidity; but, upon heating, a copious white precipitate is thrown down. This particular precipitate we did not examine more closely, but its nature may be inferred from evidence to be cited later. It undoubtedly consists either of basic mixtures or of antimonious oxide, according to the amount of sodium carbonate used and the thoroughness of the boiling.

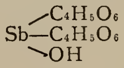
Attempts were made to prepare definite salts of antimonio-tritartaric acid, but unsuccessfully. Barium carbonate dissolves in a solution of the acid with brisk effervescence, but, upon standing, crystals of ordinary barium tartrate were deposited. The antimony in this case remained dissolved undoubtedly as the normal tritartrate. In another experiment a solution of the acid was rapidly neutralised with barium carbonate, and subsequently precipitated by alcohol. The copious white precipitate was washed with alcohol, air dried, and partially analysed. So far as ascertained its composition agrees with the formula $Sb_2(C_4H_4O_6)_3.4BaC_4H_4O_6.3H_2O$. It is probably a mixture.

	Found.		Calculated.
Sb	12.47		12.77
Ba	28.27	29.06	29.17
Water at 150°	2.45		2.87

Second. It has already been stated that a saturated solution of antimonious oxide in tartaric acid does not crystallise. Such a solution (marked 1 in the previous table) was evaporated to dryness and the dry product was analysed. The results were as follows:

Sb	27.53
C	18.31
H	2.96
H_2O at 105°	10.92

This analysis is of dubious value. The compound may not have been definite, and the figures agree sharply with no probable formula. The antimony and carbon give a ratio corresponding to seven molecules of acid to four atoms of metal, and suggest the existence of a compound having the formula $Sb(OH)H_2(C_4H_4O_6)_2$. Such a formula, which may be written structurally



$$Sb\begin{cases} C_4H_5O_6 \\ C_4H_5O_6 \\ OH \end{cases}$$

is also indicated by Peligot's analysis of his "hyperacid tartrate," but it is not clearly proved. It is also further suggested by the following reaction:

A solution containing the foregoing salt was mixed with alcohol. The usual white precipitate was washed with alcohol and air-dried over sulphuric acid. Its composition is clearly represented by the formula $Sb_2(C_4H_4O_6)_2O.6H_2O$.

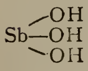
	Found.			Calculated.
Sb	36.88	36.22	36.58	36.37
C	13.56	13.90	13.56	14.54
H	2.65	2.72	2.47	3.03
H_2O at 155°	16.31	...	...	16.36

A portion of this was redissolved in water, and the solution was left to evaporate. No crystals formed, but the liquid dried up to a yellowish, scaly mass, containing 16.39 per cent. of water. Evidently no change in composition had occurred. Heated to 170° the salt lost another molecule of water, leaving two molecules of $Sb \equiv C_4H_3O_6$.

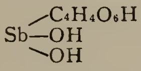
Actual loss at 170°, 19.28 per cent. Theoretical, 19.09.

A similar precipitate was also examined by Peligot, who dried his product at 160° and estimated only carbon and hydrogen. From his results the formula $SbC_4H_3O_6$ has been inferred, as well as the existence of an acid salt $SbC_4H_5O_7$.[1] The latter compound, however, he never actually obtained; and the only evidence of its existence and properties was published from this laboratory some four years ago.[2]

If now we compare the formulæ of our two acid salts (using our hypothetical formula for the second) with those of the two alcoholic precipitates, certain obvious relations will appear. There ought plainly to be two series of antimony tartrates, one acid and one neutral; the first derived from orthoantimonious acid, $Sb(OH)_3$, and the other from antimonious oxide, Sb_2O_3. The formulæ should be as follows, neglecting water of crystallization:



1.



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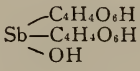

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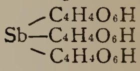

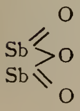

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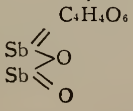

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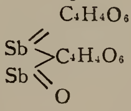
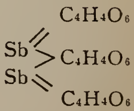


6.



Of these, numbers 3, 5 and 6 we have actually obtained in definite condition, and number 2 we have shown to be probable. The latter is related to the neutral ditartrate just as antimonio-tritartaric acid is related to the tritartrate, and the name of antimonio-ditartaric acid may fitly be applied to it. By precipitation with alcohol it yields a neutral ditartrate, precisely as number 3 by a similar reaction yields number 6. The formula, doubled, and with five molecules of water added, is found in all reference works upon chemistry as that of Peligot's hyperacid tartrate.

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[1] Commonly written $C_4H_4H(SbO)O_6$.

[2] Clarke and Stallo, this Journal, **2**, 319.

The hypothetical compound numbered 1 in the foregoing schedule we did not obtain. Number 4, the monotartrate, we attempted to investigate, but with only partial success. After a number of failures, which resulted in the formation of the neutral ditartrate, we prepared a quantity of antimonious hydroxide, which we dissolved to saturation in aqueous tartaric acid. This solution yielded a precipitate with alcohol which was comparatively insoluble in water, and which, air-dried, had the subjoined composition:

	Found.		Calculated for $Sb_2(C_4H_4O_6)O_2.2H_2O$.
Sb	53.62	53.84	52.63
C	6.43	5.38	10.52
H	1.65	1.51	1.75
H_2O at 160°	7.79		7.89

It will at once be seen that the analysis, though suggestive, is highly unsatisfactory. It merely emphasises the probability that the compound sought for exists. The white precipitate described by Berzelius had similar properties as regards insolubility, and his formula for it, translated into modern notation, agrees with ours. On the antimonyl hypothesis its formula is found in works of reference as $C_4H_4(SbO)_2O_6$. It needs, however, further investigation.

In all essential particulars the salt which we call antimonioditartaric acid behaves much like the corresponding tri-compound. It is strongly acid, effervesces with carbonates, and is not precipitated by alkalies in the cold. Its solution, saturated with barium carbonate and precipitated by alcohol, behaved precisely like that of the tri-acid, but the curdy white precipitate had a different composition. A partial analysis gave results agreeing with $Sb_2(C_4H_4O_6)_2O.3BaC_4H_4O_6.11H_2O$.

	Found.		Calculated.
Sb	15.33		14.94
Ba	26.06	26.63	25.58
H_2O at 150°	12.66		12.32

This too is most probably a mixture, although both it and the corresponding tri-acid precipitate may be weak double compounds.

In order to get further evidence concerning the nature of the acid compounds, we neutralised a solution of the di-acid with sodium carbonate. The liquid, which remained perfectly clear, was then mixed with alcohol. At first it became turbid, and later it separated into two fluid layers, both clear, and both containing antimony. The lower layer was syrupy, and contained most of the sodium; it was accordingly drawn off, and evaporated at the ordinary temperature of the air over sulphuric acid. It slowly dried up to an amorphous, gummy mass, which yielded a yellowish powder. This product we analysed. Although, under the circumstances, we could hardly expect a definite compound, our figures approximate to what is required by the empirical formula, $2Sb(OH)_3.3Na_2C_4H_4O_6.3H_2O$.

	Found.		Calculated.
Sb	24.66	25.00	24.54
Na	13.48		14.11
C	15.64	15.77	14.72
H	2.62		2.45
H_2O at 150°	11.66		11.04

This compound is probably definite, although we may have failed to determine exactly the right formula. It is readily soluble in water, and very faintly acid towards litmus paper. Its solution is stable even upon boiling, but is precipitated, when hot, by alkaline carbonates.

Another portion of the antimonio-ditartaric acid solution was exactly neutralised by sodium carbonate and boiled. A heavy precipitate fell, which we collected and dried over sulphuric acid. To the filtrate more sodium carbonate was added, and a second boiling threw down a second precipitate. Both precipitates, 1 and 2, were analysed.

	I.		II.
Sb	47.87	47.28	84.25
C	3.96	4.24	...
H	3.44	3.21	...
H_2O, 155°	22.30		4.80

The second product is evidently antimonious oxide mixed with a little hydrate. The pure oxide contains 83.33 per cent. of metal. The first precipitate approximates roughly to a tartrate having the formula $Sb_4O_5(C_4H_4O_6).12H_2O$, analogous to the sulphate $Sb_4O_5(SO_4)$, the chloride $Sb_4O_5Cl_2$, etc. Doubtless such a tartrate exists, and might be prepared in a state of purity by proper precautions. It should contain 51.95 per cent. Sb, 5.20 per cent. C, 3.03 per cent. H, 23.37 per cent. H_2O. Our results, however, only indicate the probability of such a basic salt, formed by the partial precipitation of the higher tartrates, as a step in the reduction of the latter to oxide.

With the neutral[1] ditartrate of antimony one more suggestive experiment was tried. Its solution was cautiously mixed with dilute sulphuric acid to incipient turbidity, and then immediately precipitated by alcohol. The precipitate, which was white, contained sulphuric and tartaric acids, antimony and water.

	Found.	
Sb	33.56	
SO_4	25.48	25.52
H_2O at 110°	12.31	

A compound having the formula $Sb_2(C_4H_4O_6)(SO_4)_2.7H_2O$, would require 33.99 per cent. Sb, 27.19 per cent. SO_4, and 17.84 per cent. H_2O. A loss of $5H_2O$ would amount to 12.75 per cent. Our figures, however, here as in several other cases, are merely sufficient to establish a probability which may serve as a basis for future investigations. It may be regarded as practically certain that mixed salts of antimony are possible, and that sulphato-tartrates, etc., may be obtained by careful and systematic trial. Want of time precluded us from working farther in this direction.

The foregoing results, taken altogether, establish certain points pretty clearly. First, contrary to Peligot's views, antimony forms perfectly normal tartrates, in which it acts like any other trivalent metal, and in which the assumption of an antimonyl radicle, SbO, is entirely inadmissible. The other tartrates of antimony fall naturally into series, in which we sometimes find the atoms Sb and O united in accordance with Peligot's hypothesis, but not in such a way as to give the latter any validity. In all such cases the SbO group is not to be regarded as a distinct radicle, but rather as an incident in a series; a mode of union found in many other basic compounds of other metals for which no special explanation has ever been thought necessary. In the tartar emetics we have a set of salts which may or may not be interpreted on the antimonyl theory, as was shown in this laboratory some years ago, but which are best explained by regarding them as derived from a complex tartrantimonious acid, to which may be assigned either of the two formulæ given below :

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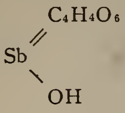
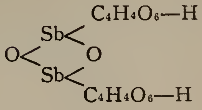
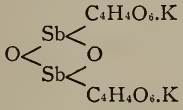
[1] The word "neutral" is inexact, but serves provisionally to indicate those tartrates of antimony which contain no replaceable hydrogen. Some of them are really basic.

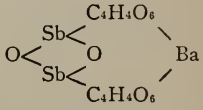


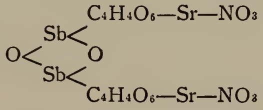
or



The first formula was adopted in the paper from this laboratory which we previously cited, but the latter is suggested by the fact that tartar emetic, as usually written, contains only half a molecule of water, and that therefore its formula should be doubled. On this plan the tartar emetics of barium and potassium may be formulated as below, and Kessler's double salt of strontium tartar emetic and strontium nitrate becomes easily explainable also.







In the course of our present investigation we have done some work upon this class of compounds, and notably as follows : A quantity of silver tartar emetic was dissolved in boiling water and precipitated by the addition of amyl iodide. Silver iodide was thrown down, the solution was instantly filtered, and upon cooling white brilliant crystals were deposited. These were insoluble in water and too small for us to determine their form. Analysis gave a composition best represented by the empirical formula $2Sb_2(C_4H_4O_6)O_2.Ag_2C_4H_4O_6.3H_2O$.

	Found.		Calculated.
Sb	37.37	38.54	38.15
Ag	17.19		17.17
C	11.21	11.26	11.45
H	1.15	1.21	1.42
H_2O, at 150°	3.43		4.29

Although the agreement here is very close, and the preparation of the salt, repeated several times, gave a perfectly uniform and apparently definite product, the formula cannot be regarded as certain. Our difficulty is that a similar experiment with ethyl iodide gave a salt of similar appearance but of different composition, as follows:

Sb	33.37
Ag	21.61
C	11.86
H	1.16
H_2O	4.44

Possibly this preparation, which we made only once, contained unaltered silver tartar emetic. At all events, uncertainty exists, and further investigation is necessary. If the formula given above should prove to be correct it would relate the compound structurally to the salts $Sb_4O_5Cl_2$, $Sb_4O_5(SO_4)$, etc.

In conclusion, we may describe the following new tartrantimonites:

Aniline tartrantimonite, $SbC_4H_5O_7.C_6H_7N$, was obtained by treating the barium salt with a solution of aniline sulphate. It crystallises very easily in long white prisms, sometimes discolored by traces of oxidation products, and has a specific gravity of 1.890 at 11°. It yielded 31.74 per cent. of antimony, which is exactly the theoretical amount.

The quinine and atropine tartar emetics were prepared in a similar manner by Mr. Karl W. Langenbeck. Both salts were amorphous, yellowish, translucent masses. The quinine salt was anhydrous; the atropine salt contained two molecules of water. The analytical data are subjoined:

Quinine Salt.	Found.		Calculated.
Sb	19.63	19.76	19.70

Atropine Salt.	Found.	Calculated.
Sb	19.88	19.67
H_2O	5.62	5.90

Contributions from the Chemical Laboratory of Harvard College.[1]

XXXI.—ON CERTAIN SUBSTITUTED ACRYLIC AND PROPIONIC ACIDS.

By C. F. Mabery and F. C. Robinson.

β-dibromacrylic acid, unlike the isomeric α-acid, will not unite with bromine at ordinary temperatures. After standing twelve days, a solution of the acid with bromine in chloroform was not bleached, and by slow evaporation of the solution, crystals were deposited which melted at 86°, the melting point of dibromacrylic acid. At 100° the addition of bromine was easily accomplished. When pure dibromacrylic acid was heated in a closed tube with undiluted bromine in slight excess over the calculated amount, for one or two hours, tetrabrompropionic acid was formed in nearly the theoretical quantity. The excess of bromine was removed by evaporation from the crude product, which was purified by pressure in filter-paper and crystallisation from carbonic disulphide and chloroform. From a concentrated solution in carbonic disulphide it crystallises by slow evaporation in oblique prisms. It is somewhat soluble in hot water, from which it separates at first as an oil; but on further cooling it crystallises in thick prisms. On boiling an aqueous solution of the acid it is rapidly decomposed, imparting a milky appearance to the solution, probably from the formation of tribromethylen. Melting point 118°–120°. Its composition was determined by the following analyses.

I. 0.2149 gram of the substance gave by Carius' method 0.4169 gram AgBr.

II. 0.1639 gram of the substance gave 0.3145 gram AgBr.

III. 0.8899 gram of the substance gave 0.2857 gram CO_2 and 0.0478 gram H_2O.

	Calculated for $C_3H_2Br_4O_2$.	Found.		
		I.	II.	III.
Br	82.04	82.55	81.76	
C	9.23			8.76
H	.51			.60

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[1] The work contained in papers XXXI and XXXII was done in connection with the summer course of instruction in chemistry for 1882.—C. F. M.

The barium, calcium, and potassium salts of this acid were made and analysed. We were unable to prepare the silver salt in a form sufficiently pure for analysis. Argentic bromide began to separate even in the dark as soon as the salt was formed.

Baric tetrabrompropionate, $Ba(C_3HBr_4O_2)_2.\frac{1}{2}H_2O$? To prepare this salt, a solution of the acid was saturated with baric carbonate, filtered, and allowed to evaporate spontaneously at the ordinary temperature.

From the concentrated solution the salt crystallised in flat prisms, which were very soluble in water. In aqueous solution the salt is permanent when exposed to the air at ordinary temperatures, but it is rapidly decomposed by heat. In the following determinations of the water of crystallisation, in each case the salt was dried to a constant weight in the air and then heated until constant at 80°.

I. 1.2784 grams of the air-dried salt lost 0.0090 gram H_2O at 80°.
II. 1.0862 grams of the air-dried salt lost 0.0081 gram H_2O at 80°.
III. 1.2403 grams of the air-dried salt lost 0.0087 gram H_2O at 80°.

	Calculated for $Ba(C_3HBr_4O_2)_2.\frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
H_2O	.96	·7	·7	·75

1.0762 grams of the salt dried at 80° gave 0.2747 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_4O_2)_2$.	Found.
Ba	14.97	15.01

Calcium tetrabrompropionate, $Ca(C_3HBr_4O_2)_2.H_2O$. When an aqueous solution of the acid was neutralised with calcic carbonate in the cold and evaporated at the ordinary temperature, the calcium salt separated from the concentrated solution in clusters of microscopic prisms, which were much less soluble in water than the corresponding barium salt. The air-dried salt contained one molecule of water of crystallisation, which was given up at 80°.

I. 1.1413 grams of the air-dried salt gave 0.0215 gram H_2O at 80°.

II. 1.1087 grams of the air-dried salt gave 0.0205 gram H_2O at 80°.

III. 1.0948 grams of the anhydrous salt gave on ignition with H_2SO_4 0.1895 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_4O_2)_2.H_2O$.	Found. I.	Found. II.
H_2O	2.15	1.88	1.85

	Calculated for $Ca(C_3HBr_4O_2)_2$.	Found.
Ca	4.89	5.09

Potassic tetrabrompropionate, $KC_3HBr_4O_2.2H_2O$. By the action of an aqueous solution of potassic carbonate on the acid a neutral solution was obtained, from which by spontaneous evaporation the potassium salt was deposited in the form of clustered needles. This salt is very soluble in water and permanent in the air at ordinary temperatures, but rapidly decomposed by heat. The air-dried salt gave up its water of crystallisation over sulphuric acid.

I. 1.1571 grams of the air-dried salt lost over H_2SO_4 0.0882 gram H_2O.

II. 1.1304 grams of the air-dried salt lost over H_2SO_4 0.0858 gram H_2O.

III. 1.0354 grams of the anhydrous salt gave on ignition with H_2SO_4 0.2165 gram K_2SO_4.

	Calculated for $KC_3HBr_4O_2.2H_2O$.	Found. I.	Found. II.
H_2O	7.76	7.62	7.59

	Calculated for $KC_3HBr_4O_2$.	Found.
K	9.14	9.39

When heated in aqueous solution the barium salt was easily decomposed with the separation of an oil which distilled readily with steam. Since tribromethylen was the only substituted hydrocarbon that could be derived from tetrabrompropionic acid under these conditions, it was converted directly into pentabromethan. The salt was distilled with an excess of baric hydrate, and the oily distillate absorbed by bromine water. A solid residue was left after evaporation of the excess of bromine, which melted at 53° when purified by crystallisation from alcohol, and on analysis gave the required percentage of bromine.

0.0918 gram of the substance gave 0.2041 gram AgBr.

	Calculated for C_2HBr_5.	Found.
Br	94.12	94.61

Carbonic dioxide was evolved in this decomposition, and the retort residue contained baric bromide in large quantity. It may therefore be expressed by the following equation:

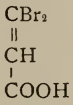
$$Ba(C_3HBr_4O_2)_2 = 2C_2HBr_3 + BaBr_3 + 2CO_2.$$

On standing with an alcoholic solution of potassic hydrate, a molecule of hydrobromic acid was eliminated from the acid with the formation of tribromacrylic acid, according to the equation:

$$C_3H_2Br_4O_2 + 2KOH = KC_3Br_3O_2 + KBr + H_2O.$$

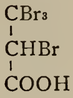
Tribromacrylic acid was recognised by its melting point, 118°, and by its crystalline form.

If the structure of β-dibromacrylic acid[1] is represented by the formula,



$$\begin{array}{c} CBr_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

the bromine addition-product would have the form,



$$\begin{array}{c} CBr_3 \\ | \\ CHBr \\ | \\ COOH \end{array}$$

The above statement concerning the behavior of β-dibromacrylic acid towards bromine holds true with regard to chlorine. Although no action takes place at ordinary temperatures, when chlorine is passed through the melted acid the addition-product is formed without difficulty. The resulting dichlordibrompropionic acid will be submitted to further examination.

We have also tried the action of hydrobromic acid upon β-dibromacrylic acid, but as yet our results are as unsatisfactory as those of Fittig and Petri.[2] The product melted at about 53° and gave a percentage of bromine which showed that it contained much unaltered dibromacrylic acid. Nevertheless, by prolonged heating, we hope to obtain the tribrompropionic acid in a form sufficiently pure to enable us to study its properties.

Several attempts were made to obtain an addition-product by the action of bromine monochloride on brompropiolic acid. A substance was formed which melted quite constant at 110°–112°; but the results of analyses indicated that it was a mixture of the chlorine and bromine addition-products. In one experiment a product was obtained which melted at 102°–105°, and the percentage of bromine was very considerably increased. There is little doubt that the addition would take place, provided the bromine monochloride could be obtained in a state of purity under conditions necessary to form addition-products.

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[1] H. B. Hill. This Journal, **4**, 276, and Proceedings American Academy, **17**, 153.

[2] Annalen der Chemie, **195**, 73.

When brompropiolic acid is dissolved in chloroform saturated at 0° with chlorine, and allowed to stand for some time, the chlorine is absorbed with the formation of bromdichloracrylic acid.

XXXII.—ON THE DECOMPOSITION OF CHLORTRIBROMPROPIONIC ACID BY ALKALINE HYDRATES.

By C. F. Mabery.

In a previous paper by H. C. Weber and myself,[1] some experiments were mentioned in which we had attempted to determine the decomposition-products of chlortribrompropionic acid. Although our results were not entirely satisfactory, we were unable to verify them on account of the limited time at our disposal. Since the necessary material could be obtained without difficulty, it seemed worth while to define this reaction with greater precision. This work was undertaken by Mr. R. D. Wilson, who found that on prolonged heating with baric hydrate in aqueous solution, chlortribrompropionic acid was completely decomposed, according to the equation,

$$Ba(C_3HClBr_3O_2)_2 = 2C_2HClBr_2 + BaBr_2 + 2CO_2.$$

For identification the volatile product of the distillation was converted into chlortetrabromethan. It was caught in bromine water, the excess of bromine allowed to evaporate, and the oil which separated cooled to 0°. The solid thus obtained was purified by crystallisation from alcohol, and its composition determined by analysis.

0.1556 gram of the substance gave 0.3657 gram AgBr+AgCl.

	Calculated for C_2HClBr_2.	Found.
Cl + 4Br	93.42	93.30

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[1] This Journal, **4**, 106, and Proceedings American Academy, **17**, 209.

Since this substance melted at 33°, it was probably identical with the chlortetrabromethan, melting point 32°–33°, obtained by Wallach and Bischof,[1] from the decomposition of β-dichloracrylic acid.

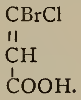
$$CCl_2 = CH - COOH.$$

This acid gave chloracetylen, $CCl \equiv CH$, which by the addition of bromine formed chlortetrabromethan,

$$\begin{array}{l} CHBr_2 \\ | \\ CClBr_2 \end{array}$$

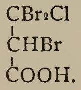
By the action of potassic hydrate in alcoholic solution upon chlortribrompropionic acid, the elements of hydrochloric acid were eliminated, with the formation in small quantity of tribromacrylic acid.

From the evident analogy between chlorbromacrylic acid, from which chlortribrompropionic was made, and β-dibromacrylic acid, the structure of chlorbromacrylic acid[2] is probably,



$$\begin{array}{l} CBrCl \\ \| \\ CH \\ | \\ COOH. \end{array}$$

Chlortribrompropionic acid would then have the form,



$$\begin{array}{l} CBr_2Cl \\ | \\ CHBr \\ | \\ COOH. \end{array}$$

XXXIII.—ON THE PRODUCTS OF THE DRY DISTILLATION OF WOOD AT LOW TEMPERATURES.

By Charles F. Mabery.

In the manufacture of acetic acid by the dry distillation of wood at low temperatures, as it is conducted by Dr. E. R. Squibb, of Brooklyn, N. Y., an oil heavier than water collects during the distillation in considerable quantities. Upon examination, Professor H. B. Hill[3] found that this oil contained a large percentage of furfurol, and that by the action of alkalies upon it a small quantity of pyroxanthin was formed. Further information concerning the more volatile products of the distillation therefore seemed desirable; and since different portions of the crude methyl alcohol were kindly placed at my disposal by Dr. Squibb, I undertook an examination of its constituents.

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[1] Annalen der Chemie, **203**, 89.

[2] H. B. Hill, this Journal, **4**, 276; and Proceedings American Academy, **17**, 153.

[3] This Journal, **3**, 33; and Proceedings American Academy, **16**, 102.

The composition of crude wood spirit has frequently been made the subject of investigation within a few years. Beside methyl alcohol and methyl acetate, which constitute the greater part of the product in the ordinary process of distillation, acetic aldehyde, acetic acid, aceton, acetal, dimethylacetal, methylethylketone, and allyl alcohol have been found in smaller quantities. Traces of the higher ketones have been detected in the less volatile portions, and in the high boiling oils small quantities of the aromatic hydrocarbons toluol, xylol, and cumol.

A study of the product under consideration shows that it has essentially the same composition. Its distinctive characteristic consists in different quantitative proportions of several constituents, probably due to the low temperature at which the first distillation was conducted. It also contains methyl formiate, which has not hitherto been recognised as a constituent of wood spirit.[1]

Three portions were selected for examination. The first portion (*a*) was collected at the beginning of the distillation, the second (*b*) after several hundred gallons had distilled, and the third (*c*) when the distillation of methyl alcohol was well advanced. Each portion was bright yellow in color, and from (*a*) and (*b*) a sharp penetrating odor was emitted. Since various attempts to remove the small percentage of water by desiccation were unsuccessful, the product was fractional as it was received. Anhydrous cupric sulphate absorbed only a small fraction of the water, even after standing several weeks, and fused potassic carbonate produced a decomposition, as shown by the color changing to a dark brown, with the formation of a yellow precipitate on standing. In the fractional distillation very satisfactory results were obtained, both in the separation of the different fractions and in economy of time, by the use of Hempel's[2] device for condensation.

The following table contains the results of the tenth fraction of each portion expressed in percentages. To insure a more complete condensation of the volatile products in (*a*), after passing through a Liebig's condenser, the distillate was cooled by a freezing mixture. Considerable gas escaped condensation at the beginning of the distillation, but it was found to consist chiefly of carbonic dioxide.

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[1] Krämer and Grodzky succeeded in isolating formic acid in small quantity from the oil obtained by adding sulphuric acid to the mother liquor of *Holzessig*, after removing the greater part of the acetic acid as sodic acetate. (Berichte der deutschen chemischen Gesellschaft, **11**, 1356.)

[2] Zeitschrift für analytische Chemie, **20**, 502.

The residue of the distillation in each case contained the greater part of the water, though in (*a*) it consisted chiefly of methyl alcohol. In (*b*) approximately one-half of the residue consisted of the higher boiling oils, and in (*c*) it was composed beside water of furfurol and an oil of low specific gravity. The constituents of the various fractions will be described in detail.

(*a*)		(*b*)		(*c*)	
Temperatures.	Percentages.	Temperatures.	Percentages.	Temperatures.	Percentages.
20°–25°	2.1				
25 –30	1.5				
30 –40	1.				
40 –50	1.				
50 –52	1.6				
52 –54	9.3	Below 54°	3.		
54 –56	62.8		74.1		
56 –60	7.3		3.6	Below 63°	4.7
Above 60°	6.7	60°–70°	3.7	63°–65°	2.5
		Above 70°	9.9	65°–68°	57.9
				Above 68°	31.4
Loss	6.7		5.7		3.5

Acetic Aldehyde.

In (*a*) the fraction that came over between 20° and 25° was very soluble in water, and it gave the penetrating odor characteristic of acetic aldehyde. This substance was also recognised in that portion of (*b*) which distilled below 54°, and in the fraction below 63° in (*c*). It formed a compound with acid sodic sulphite, crystallising in flat prisms, which were very soluble in water. In order to establish its identity, an aqueous solution of the fraction 20°–25° was boiled with an excess of silver oxide, filtered, and concentrated by evaporation. On cooling, silver acetate crystallised in characteristic forms, which, on analysis, gave the required percentage of silver.

I. 0.2222 gram of the substance gave on ignition 0.1432 gram Ag.

II. 0.3167 gram of the substance gave on ignition 0.2050 gram Ag.

	Calculated for $AgC_2H_3O_2$.	Found.	
		I.	II.
Ag	64.68	64.43	64.73

According to Krämer and Grodzky,[1] in the manufacture of wood spirit, acetic aldehyde may usually be found in the first portions of the distillate. It is rarely present in large quantities, since, as they assert, the greater part is converted into dimethylacetal during the distillation.

Methyl Formiate.

This substance was isolated from the fractions 25°–30° and 30°–40°. On the addition of water an oil separated, which was purified by fractional distillation. There were thus obtained 8 grams of a substance which distilled between 30° and 35°. It was saponified by boiling with an excess of plumbic hydrate, and the composition of the plumbic formiate determined by analysis.

I. 0.5214 gram of the substance dried over H_2SO_4 gave on ignition with H_2SO_4 0.5296 gram $PbSO_4$.

II. 0.2900 gram of the substance gave 0.2960 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.	
		I.	II.
Pb	69.69	69.42	69.71

The presence of formic acid, and the quantity of the distillate which collected between 40°–50°, suggested the possible formation of methylal. This fraction was therefore treated with an equal volume of water, and the oil which separated boiled with plumbic hydrate to decompose the methyl formiate. After drying with fused calcic chloride, the residue distilled above 50°. In another attempt to isolate methylal, 2000 grams of (*a*) were fractioned, and the distillate below 50° examined according to Dancer's method[2] for the separation of dimethylacetal. As in the first experiment, the residue distilled at a temperature far above the boiling point of methylal, which seemed to indicate that this substance could not have been formed in any appreciable quantity.

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[1] Berichte der deutschen chemischen Gesellschaft, **9**, 1920.

[2] Annalen der Chemie, **132**, 240.

Methyl Acetate.

Since the fractions 50°–52° and 52°–54° gave reactions for aldehyde and acetone, they were evidently a mixture of these substances with methyl acetate. The greater part of the methyl acetate in (*a*) and (*b*) was collected in the fraction 54°–56°, which boiled constant at 54.5°–55.5° (Bar. 769.5 mm.). To determine approximately the percentage of methyl alcohol in this fraction, 655 grams were saponified with potassic hydrate, and distilled. After drying with fused potassic carbonate and distilling off the methyl alcohol, there were obtained 255 grams, which came over between 66° and 67° (Bar. 769.5 mm.), or 92 per cent. of the amount required from the weight taken of methyl acetate. In repeating this saponification in a dilute solution of methyl acetate, with a potassic hydrate solution of known strength, the excess of alkali was titrated with standard sulphuric acid, and the percentage of methyl acetate calculated from the amount of potassic hydrate required to decompose it. This method gave 99.2 per cent. of pure methyl acetate.

Methyl Alcohol.

Although a small amount of methyl alcohol was contained in the higher fractions of (*a*) and (*b*), it was evidently condensed for the most part in the fraction 65°–68° of (*c*). This fraction was slightly yellow in color, but no further attempts were made to determine its purity than an estimation of the percentage of acetone, which will presently be described.

Dimethylacetal.

The formation of dimethylacetal during the dry distillation of wood for the preparation of methyl alcohol was not observed until 1864, probably because of the small difference between its boiling point (64°) and that of methyl alcohol. After removing the methyl alcohol and acetone, Dancer[1] succeeded in separating a product which proved to be identical with dimethylacetal, made by heating methyl alcohol with acetic aldehyde. Krämer and Grodzky[2] state that it has since been recognised as a constant constituent of wood spirit. Its formation is probably due to the high temperature of the distillation, which enables the aldehyde to act upon the methyl alcohol. From the large percentage of aldehyde in the product under consideration, it would seem that this reaction had not taken place to any extent. Since an examination of the distillate below 65° in (*c*) failed to reveal the presence of dimethylacetal, a second portion of 2000 grams was fractioned, the lower fraction saponified and distilled over calcic oxide. The small amount of residue left after removing the methyl alcohol with calcic chloride, distilled at 57°–58°, was readily miscible with water, and its reactions in general were characteristic of acetone. Dimethylacetal could not therefore have been formed in quantity sufficient for identification.

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[1] Annalen der Chemie, **132**, 240.

[2] Berichte der deutschen chemischen Gesellschaft, **9**, 1920.

Acetone.

The first quantitative experiments on the influence of acetone upon the commercial value of methyl alcohol were made by Krämer and Grodzky.[1] They determined the quantity of dimethylaniline which could be obtained from a given weight of pure methyl alcohol, and also from methyl alcohol containing different amounts of acetone. Their results seemed to show that the yield was very considerably diminished if the quantity of acetone exceeded one per cent. Since crude wood spirit always contains a much higher percentage, it must be specially purified for the preparation of dimethylaniline.

Various methods, dependent either upon the physical or chemical properties of methyl alcohol, have been proposed for testing its purity. Krell[2] suggested a determination of the amount of methyl iodide which could be obtained by treating a given quantity of the alcohol with phosphorous iodide. In the hands of a skilful analyst the percentage of methyl alcohol may be accurately determined by this method; but, as Krämer remarked, it does not account for the nature of the impurities, and it is not sufficiently expeditious. To overcome these objections, Krämer[3] took advantage of the formation of iodoform from acetone. In his modification of Lieben's reaction[4] the formation of iodoform from ethyl alcohol and acetic acid is avoided, and acetic aldehyde is only partially decomposed.

According to Krämer's method a mixture of 10 cc. of a normal sodic hydrate solution, 5 cc. of a double-normal iodine solution and 1 cc. of the alcohol to be tested is shaken in a graduated cylinder with 10 cc. of ether. 5 cc. of the ether solution are withdrawn with a pipette, evaporated on a weighed watch-glass, and the residue weighed after drying in a warm desiccator. To obtain the weight of acetone in 1 cc. of the alcohol, the weight of iodoform is multiplied by .28 if there are 9.5 cc. of the ether solution.

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[1] Berichte der deutschen chemischen Gesellschaft, **13**, 1005.

[2] *Ibid.* **6**, 1310.

[3] *Ibid.* **13**, 1000.

[4] Annalen der Chemie, Suppl. VII., 218, 377.

The percentage of acetone in several fractions, as determined by this method, is giving in the following table.[1] Since in each determination from 9 cc. of the ether solution 5 cc. were evaporated, the weight of iodoform was multiplied by .27 for the weight of acetone.

Fraction treated.	Specific Gravity.	Weight of Iodoform.	Weight of Acetone.	Percentage of Acetone.
54°–56° (*a*)	0.935	0.0359	0.0097	1.04
Below 54° (*b*)	0.930	0.0648	0.0175	1.88
54°–56° (*b*)	0.935	0.0638	0.0182	1.95
Methyl Alcohol				
from 54°–56° (*b*)	0.805	0.0914	0.0247	3.07
56°–60° (*b*)	0.830	0.0802	0.0217	2.66
65°–68° (*c*)	0.820	0.1037	0.0280	3.41

Although the quantity of acetone in the product under consideration is sufficiently large to render further purification necessary, it is evidently much smaller than is usually observed in commercial wood spirit.

Allyl Alcohol.

The occurrence of allyl alcohol as a product of the distillation of wood was first mentioned by Aronheim,[2] and soon afterward Krämer and Grodzky[3] stated that small quantities of it may always be found in the higher fractions. In examining the aqueous part of the residue in (*c*) for this substance, after removing the water, a small amount of an oil was left, with a boiling point somewhat higher than that of allyl alcohol. It absorbed bromine readily, with the formation of a product which boiled much too low for dibromallyl alcohol, and oxidation with nitric acid gave only oxalic acid. Since from the results of Krämer and Grodzky it is usually present in wood spirit, in quantity not exceeding two tenths of one per cent., it is evidently possible that the small amount contained in 2000 grams might escape observation.

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[1] In several instances the fraction was boiled with silver oxide before testing for acetone, but this seemed to have no appreciable effect on the quantity of acetone indicated by the iodoform reaction.

[2] Berichte der deutschen chemischen Gesellschaft, **7**, 1381.

[3] *Ibid.* **7**, 1492.

High Boiling Oils.

Although the composition of the higher boiling fractions was not determined with sufficiently desirable accuracy, a brief description of my attempts to isolate substances which have already been found in the less volatile portions of wood spirit may have some interest. It has already been mentioned, that beside water these fractions consisted of an oil heavier and an oil lighter than water. The heavier oil was composed chiefly of furfurol, though, as well as the water and lighter oil, it contained pyroxanthine in small quantity, which could be precipitated by the addition of sodic hydrate. 2000 grams of (*c*) gave 45 grams of the lighter oil, which was pale yellow when freshly distilled, but it turned dark brown on standing. In attempting to fraction it, a constant boiling point could not be obtained between 75° and 200°. About two grams of a substance distilled between 75° and 85°, which formed crystals with acid sodic sulphite, indicating the presence of methylethylketone; but the quantity obtained was insufficient for analysis. The penetrating odor observed in the distillate between 95° and 105° was characteristic of the allyl compounds. It was possibly due to a trace of allyl acetate, since after heating with sodic hydrate and neutralising the solution a qualitative test for acetic acid was obtained with ferric chloride. This oil distilled for the most part between 150° and 200°. Finding, however, that a constant boiling point could not be obtained with the supply of substance at my command, I did not consider it worth while to fraction the amount of material necessary to obtain the oil in large quantity.

The important characters of this product, as they have appeared in the course of the preceding examination, may be summarised as follows:

1. The high percentage of aldehyde in (*a*), of methyl acetate in (*a*) and (*b*), and of methyl alcohol in (*c*).
2. Presence of methyl formiate.
3. Absence of dimethylacetal.
4. Small percentage of acetone.
5. General purity of the product.

XXXIV.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

TWELFTH PAPER.

CERTAIN PARABROMBENZYL COMPOUNDS.[1]

By C. Loring Jackson and G. T. Hartshorn.

In a previous paper of this series a number of parachlorbenzyl compounds containing sulphur were described; the following paper contains a description of the corresponding compounds made from the parabrombenzylbromide.[2]

Parabrombenzylsulpho-acid, $C_6H_4BrCH_2SO_3H$.

The potassium salt of this substance was made by heating parabrombenzylbromide with an aqueous solution of neutral potassic sulphite in a flask with a return-cooler until the odor of the bromide disappeared. It was purified by crystallisation from water, and dried first *in vacuo*, and afterwards at 110°, which showed that it contained no water of crystallisation.

0.2230 gram of the substance gave, according to Carius, 0.1454 gram of argentic bromide.

0.2624 gram gave 0.1724 gram of argentic bromide, and 0.2140 gram of baric sulphate.

0.2224 gram, after evaporation with sulphuric acid, gave 0.0688 gram of potassic sulphate.

	Calculated for $C_7H_6BrSO_3K$.	Found.	
Bromine	27.67	27.75	27.96
Sulphur	11.07		11.20
Potassium	13.50	13.89	

It crystallises in narrow plates, which not infrequently reach a length of over one centimeter, and are characterised by a well-marked cleavage at right angles to their longer axis. On one occasion rhombic forms similar to those of the sodium salt of the parachlorbenzylsulpho-acid were observed. It is not freely soluble in cold water or alcohol, but its solubility in each of these solvents is much increased by heat. The solubility in water at 18° was determined as follows:

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[1] Presented to the American Academy. Communicated by the Authors.

[2] The results obtained will be found in tabular form at the end of the article.

I. 3.2760 grams of the saturated solution gave 0.2016 gram of the salt.

II. 2.7104 grams gave 0.1689 gram of the salt.

Percentage of $C_6H_4BrCH_2SO_3K$ in aqueous solution saturated at 18°:

I.	II.
6.15	6.25

To make the other salts of the sulpho-acid, the crude potassium salt was treated with a small quantity of plumbic acetate, to free it from bromide and sulphite; and, after filtering from the precipitate thus formed, the lead salt was thrown down by adding an excess of plumbic acetate, and purified by crystallisation from water. It was then suspended in water, and treated with sulphuretted hydrogen to convert it into the free acid, which was used in the preparation of the following salts.

The *Calcium Salt* $(C_6H_4BrCH_2SO_3)_2Ca$, made by warming the acid with calcic carbonate, and purified by crystallisation from water, was free from water of crystallisation.

0.4472 gram of the salt dried at 110° gave 0.1096 gram of calcic sulphate.

0.2870 gram gave 0.0715 gram of calcic sulphate.

	Calculated for $(C_7H_6BrSO_3)_2Ca$.	Found.	
Calcium	7.41	7.21	7.33

The salt crystallises in long colorless plates, and is freely soluble in water.

The *Barium Salt* $(C_6H_4BrCH_2SO_3)_2BaH_2O$ was made from the acid with baric carbonate, and purified by crystallisation from water.

0.4300 gram of the salt dried *in vacuo* lost, when heated to 110°, 0.0124 gram of water.

0.4396 gram lost 0.0123 gram of water.

	Calculated for $(C_7H_6BrSO_3)_2BaH_2O$.	Found.	
Water	2.75	2.88	2.80

0.1630 gram of dried salt gave 0.0592 gram of baric sulphate.

0.3625 gram gave 0.1314 gram of baric sulphate.

	Calculated for $(C_7H_6BrSO_3)_2Ba$.	Found.	
Barium	21.50	21.35	21.31

It crystallises in stellate groups of white needles, and is slightly deliquescent. Its solubility in water was determined as follows:

I. 4.0670 grams of the solution saturated at 18° gave 0.1649 gram of the salt.

II. 4.1510 grams gave 0.1679 gram of the salt.

Percentage of $(C_6H_4BrCH_2SO_3)_2Ba$ in aqueous solution saturated at 18°:

I.	II.
40.55	40.46

The *Lead Salt* $(C_6H_4BrCH_2SO_3)_2Pb$, made and purified as already described, was free from water of crystallisation.

0.3144 gram of the salt dried at 110° gave on combustion 0.2709 gram of carbonic dioxide, and 0.0481 gram of water.

0.2988 gram of the salt gave 0.1297 gram of plumbic sulphate.

	Calculated for $(C_7H_6BrSO_3)_2Pb$.	Found.
Carbon	23.76	23.51
Hydrogen	1.69	1.70
Lead	29.28	29.66

It crystallises in radiating groups of long white needles. Its solubility in water was determined as follows:

I. 4.3370 grams of the solution saturated at 18° gave 0.0873 gram of the salt.

II. 3.4536 grams gave 0.0691 gram of the salt.

Percentage of $(C_6H_4BrCH_2SO_3)_2Pb$ in aqueous solution saturated at 18°:

I.	II.
2.01	2.00

The *Chloride* of the *Sulpho-acid* $C_6H_4BrCH_2SO_2Cl$ was made by grinding the dry potassium salt in a mortar with phosphoric penta-chloride, and finishing the reaction by a gentle heat. The substance was precipitated on the addition of water as an oil, which solidified on standing, and was purified by crystallisation from ether or ligroine. It was dried *in vacuo* and analysed.

0.2460 gram of substance gave, by the method of Carius, 0.3000 gram of the mixture of argentic chloride and argentic bromide, and 0.2028 gram of baric sulphate.

	Calculated for $C_7H_6BrSO_2Cl$.	Found.
Chlorine and Bromine	42.85	42.50
Sulphur	11.87	11.35

It crystallises in small white prisms with a peculiar smell, similar to that of parabrombenzylbromide; but when cold it does not attack the mucous membrane, and when warmed only in a very much less degree than any of the brombenzylbromides. It melts at 115°, is essentially insoluble in water, and but slightly soluble in cold alcohol, ligroine, carbonic disulphide, and glacial acetic acid, freely soluble in all these solvents when hot, and in benzol and ether even in the cold.

Parabrombenzylsulphide, $(C_6H_4BrCH_2)_2S$.

This substance was made by boiling parabrombenzylbromide with an alcoholic solution of sodic sulphide; the reaction takes place very easily. The product obtained by distilling off part of the alcohol and precipitating with water was purified by crystallisation from alcohol. Dried *in vacuo* it gave the following results on analysis:

I. 0.1768 gram of substance gave, according to Carius, 0.1780 gram of argentic bromide.

II. 0.1807 gram gave 0.1828 gram of argentic bromide and 0.1057 gram of baric sulphate.

III. 0.2284 gram gave 0.1368 gram of baric sulphate.

	Calculated for $(C_7H_6Br)_2S$.	Found.		
		I.	II.	III.
Bromine	43.01	42.85	43.06	...
Sulphur	8.60	...	8.04	8.23

Properties.—It crystallises in large thin plates, apparently rhombic crystals, which have a tendency to turn brown in the air; the odor is aromatic, and not especially disagreeable; it melts at 58°–59°; is essentially insoluble in water, soluble with difficulty in cold alcohol, ligroine, or glacial acetic acid, but freely in each of these solvents when hot, and in ether, benzol, or carbonic disulphide.

Parabrombenzylsulphone, $(C_6H_4BrCH_2)_2SO_2$, was made from the sulphide by dissolving it in glacial acetic acid, and adding the calculated amount of chromic anhydride also dissolved in glacial acetic acid. After the action had ceased, the substance was precipitated with water, and purified by crystallisation from alcohol. It was analysed after drying at 100°.

0.1674 gram of substance gave by the method of Carius 0.1556 gram of argentic bromide and 0.0991 gram of baric sulphate.

	Calculated for $(C_7H_6Br)_2SO_2$.	Found.
Bromine	39.60	39.56
Sulphur	7.92	8.13

It crystallises in white needles, with a slight not unpleasant smell; melts at 189°, and is essentially insoluble in water, soluble only to a slight extent in cold alcohol, benzol, ligroine, and glacial acetic acid, freely soluble in all these solvents when hot, and in ether and carbonic disulphide whether cold or hot.

Parabrombenzylmercaptan, $C_6H_4BrCH_2SH$.

This substance was made by the action of parabrombenzylbromide on an alcoholic solution of potassic sulphydrate. The action took place very easily, and the product fell as an oil on the addition of water to the alcoholic solution. It was purified by distillation with steam, and solidified to a white crystalline mass after standing some time. It had a disagreeable odor, and melted at 25°, but we cannot be perfectly certain that this is the true melting point, on account of its strong tendency to pass into the disulphide on exposure to the air. The number given above, however, cannot be far from the correct one, as the sample was treated with zinc and sulphuric acid immediately before taking the melting point. It dissolves easily in all the common solvents with the exception of water and glacial acetic acid. It did not seem worth while to analyse the free mercaptan, as the results obtained from it are almost identical with those from its principal impurity, the disulphide; but instead of this, we determined its nature much more satisfactorily by converting it into the mercaptid, which was then analysed.

Parabrombenzylmercaptid, $(C_6H_4BrCH_2S)_2Hg$.

This substance was made by adding yellow mercuric oxide to the mercaptan suspended in water; after the action had ceased, the insoluble residue was purified by crystallisation from boiling alcohol, and dried at 100°.

0.2623 gram of substance gave on precipitation with sulphuretted hydrogen 0.1016 gram of mercuric sulphide.

	Calculated for $(C_7H_6BrS)_2Hg$.	Found.
Mercury	33.11	33.38

It crystallises from boiling alcohol as a light white feathery mass with a pearly lustre. It does not melt, but is decomposed and blackened at a high temperature, is essentially insoluble in water, very slightly soluble in cold alcohol, benzol, or glacial acetic acid, freely soluble in hot alcohol (the solution becomes nearly solid on cooling) and benzol, less so in hot glacial acetic acid, but freely in ether and carbonic disulphide.

Parabrombenzyldisulphide, $(C_6H_4BrCH_2)_2S_2$.

This substance was made from the mercaptan by exposure to the air, and also by acting on the parabrombenzylbromide with an alcoholic solution of sodic disulphide; the product precipitated with water was purified by crystallisation from alcohol, and dried *in vacuo.*

0.1600 gram of the substance gave by the method of Carius 0.1487 gram of argentic bromide and 0.1838 gram of baric sulphate.

	Calculated for $(C_7H_6Br)_2S_2$.	Found.
Bromine	39.60	39.57
Sulphur	15.84	15.78

It crystallises in radiating groups of white needles, and has a not unpleasant aromatic smell; melting point, 87°–88°. It is essentially insoluble in water, slightly soluble in cold alcohol, and almost insoluble in cold glacial acetic acid, but freely soluble in both these solvents when hot, and in ether, benzol, and carbonic disulphide.

The following table gives the formulas and melting points of the substances described in this paper.

Name.	Formula.	Melting point.
Parabrombenzylsulpho-acid		
Potassium Salt[1]	$C_6H_4BrCH_2SO_3K$	
Calcium Salt	$(C_6H_4BrCH_2SO_3)_2Ca$	
Barium Salt[2]	$(C_6H_4BrCH_2SO_3)_2BaH_2O$	
Lead Salt[3]	$(C_6H_4BrCH_2SO_3)_2Pb$	
Chloride	$C_6H_4BrCH_2SO_2Cl$	115°
Parabrombenzylsulphide	$(C_6H_4BrCH_2)_2S$	58°–59°
Parabrombenzylsulphone	$(C_6H_4BrCH_2)_2SO_2$	189°
Parabrombenzylmercaptan	$C_6H_4BrCH_2SH$	25°
Parabrombenzylmercaptid	$(C_6H_4BrCH_2S)_2Hg$	
Parabrombenzyldisulphide	$(C_6H_4BrCH_2)_2S_2$	87°–88°

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[1] The solution saturated at 18° contains 6.20 per cent of the salt.

[2] The solution saturated at 18° contains 40.50 per cent. of the salt.

[3] The solution saturated at 18° contains 2.00 per cent. of the salt.

XXXV.—A NEW METHOD OF PREPARING BORNEOL FROM CAMPHOR.[1]

BY C. LORING JACKSON AND A. E. MENKE.

The natural borneol (Borneo camphor), obtained from the *Dryobalanops Camphora*, is brought from the East so rarely that specimens of it can be obtained in this country or in Europe only with the greatest difficulty. Most chemists, who have studied this substance, have confined their attention therefore to the borneol obtained from ordinary camphor, which has been proved to be identical[2] with the natural product.

So far as we can find, there are but two methods of making borneol from camphor—one by the action of potassic hydrate, which is due to Berthelot;[3] the other that of Baubigny,[4] consisting in treating camphor with sodium, and separating the sodium camphor from the sodium borneol by carbonic dioxide. Both leave much to be desired, since the product of the first is a mixture of camphor and borneol, which must be purified by treatment with stearic acid, and according to Kachler[5] the yield is very small, while the second yields pure borneol, it is true, but theoretically only one-half of the camphor can be converted into borneol, although an amount of sodium is required which corresponds to the whole weight of camphor used.

In the course of some experiments on camphor, which led to no result so far as their main object was concerned, it was necessary for us to become acquainted with the reduction of camphor; but, to our great surprise, we were unable to find any description of experiments on this subject, unless the statement in Beilstein's *Handbuch der organischen Chemie*, page 1763, that sodium amalgam does not act on camphor, comes under this head. We were compelled, therefore, to experiment ourselves, with the following result: 25 grams of camphor, melting at 175°, were dissolved in moist toluol, and sodium and water added at intervals, until a sample showed the melting point of borneol, 197°–198°; the toluol was then driven off by heat, and a yellowish white mass obtained, with the smell at once like camphor and pepper, described as that of borneol. It was purified by sublimation, and analysed with the following results:

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[1] Presented to the American Academy. Communicated by the Authors.

[2] Kachler. Wien Acad. Ber. (2 Abth.). 78, July.

[3] Annales de Chimie et de Physique, ser. 3, **56**, 78.

[4] *Ibid.* ser. 4, **19**, 221.

[5] Annalen der Chemie, **164**, 75.

0.1642 gram of substance gave 0.4700 gram of carbonic dioxide and 0.1772 gram of water.

	Calculated for $C_{10}H_{18}O$.	Found.
Carbon	77.93	78.07
Hydrogen	11.69	11.98

The substance is borneol, therefore, and the reduction of the camphor takes place, as was to be expected, according to the reaction,

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} + H_2 = \underset{\text{Borneol.}}{C_{10}H_{18}O}.$$

The ease with which borneol was formed in this experiment led us to the following method for making borneol from camphor, which gives essentially the theoretical yield of nearly pure borneol with remarkably little trouble.

It consists in dissolving the camphor in about ten times its weight of common alcohol, and adding one-third[1] more than the amount of sodium calculated from the reaction. The sodium is added in pieces of somewhat less than a gram at a time, and in working with quantities not over ten grams the action can be carried on in an open flask without cooling. As soon as all the sodium has disappeared, which takes less than three-quarters of an hour with ten grams of camphor, part of the alcohol is distilled off, and water added, which precipitates crude borneol. This is freed from sodic hydrate by washing with water; after which one crystallisation from the smallest possible amount of hot alcohol is sufficient to raise its melting point to 197°, that of borneol. In this way 10 grams of camphor yielded 9.5 grams of the crude borneol, instead of 10.1 grams; that is, 94 per cent. of the theory; whereas, according to Baubigny's method, 4 grams of sodium, the amount which yielded 9.5 grams of borneol in our process, would have given only 6.6 grams.

Our method, therefore, is superior to the other two in economy, as well as in the ease and speed with which it can be conducted.

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[1] Probably a smaller excess of sodium would be sufficient.

MINERALS FROM LEHIGH COUNTY, PA.

By Edgar F. Smith.

1. *Allophane.*

About seven miles from Allentown, near the village of Ballietsville, are numerous iron mines, in which from time to time have been found white, mamillary and stalactitic incrustations upon the ore. In one of these mines a pocket was recently discovered, the inner side of which was completely covered with this coating. The latter has a mother-of-pearl-like appearance, and may be readily detached from the ore by means of a knife. Upon subjecting a portion of this material to a qualitative examination, the presence of water, alumina and silica was revealed. By strong hydrochloric acid, complete decomposition ensued. A quantitative examination yielded the following results:

H_2O	40.86 per cent.
SiO_2	21.39
Al_2O_3	35.20
$CaCO_3$ and $MgCO_3$ . . .	1.96
	99.41

Prof. Prime, in his report on the Geology of Lehigh Co., mentions the occurrence of this mineral in some of the iron mines, but gives no analytical data.

2. *Fluorite.*

About one and a half miles southeast of the above locality are the limestone quarries of Mr. Kleckner. In them have been discovered veins of beautiful fluorite and fine quartz crystals. The former mineral occurs intimately mixed with the limestone, and presents itself in the most beautiful green, purple and pink colors. Upon several specimens octahedral forms were observed, but not very distinct. It is seldom that entire crystals can be procured, since blasting is invariably necessary to reach them; consequently fragments are the result. Quantitative analyses of the purple and green varieties were made.

Purple variety:	Fl . . .	49.20 per cent.
	Ca . . .	50.87
	Fe_2O_3 . .	trace
		100.07

The mean of the specific gravities of five specimens was 3.21; ranging from 3.17–3.24. The shade of purple varied very much in the specimens examined.

Green variety:	Fl . . .	49.00 per cent.
	Ca . . .	50.91
	Fe_2O_3 . .	trace
		99.91

Sp. gr. about the same as in case of the purple. South of Emmaus in the Lehigh mountains Mr. Benj. Sadtler, Jr., found this mineral in perfect octahedra of deep purple color in a granitic rock.

3. *Zircon.*

On the farm of Jacob Stine, Esq., Upper Milford Twp., about two miles south of Macungie, are found large quartz fragments distributed over the ground surface. When these are broken, minute crystals are observed here and there in them. Close examination showed these to be perfect forms of zircon—the prism with pyramid being quite distinct; the color of these microscopic crystals varied from a cinnamon to very dark brown. In some of the quartz fragments minute leaflets of graphite and pyrite crystals were seen accompanying the zircon. Enough qualitative tests were made to identify the latter as such. Almost every piece of quartz examined contained one or more crystals of it. Their removal from the matrix was tedious and difficult. Scarcity of material prevented a quantitative examination.

4. *Wavellite, etc.*

Not more than a quarter of a mile from the above locality and upon the same farm, were found the beautiful crystals of wavellite described by Dr. N. W. Thomas and the writer, Proceedings of American Philosophical Society, March 17, 1882. The first specimens of this mineral were noticed as occurring on limonite; since the publication of the preliminary notice we have obtained, through the liberality of Mr. Stine, a number of specimens lying upon or disseminated through a jasper-like rock which overlies the iron bed. The adjacent land is covered with rock of this character. Mixed with the iron is much pyrolusite. At present the shaft, in which the most beautiful wavellite was found, is filled with debris. From the quantity of the mineral found at first, and the many points at which it was observed prior to the caving-in of the surface, we may reasonably expect to yet obtain handsome specimens. It usually occurs in beautiful, colorless, radiating nodules on the limonite or jasper-rock.

Analysis.

Al_2O_3	36.66 per cent.
P_2O_5	34.14
H_2O	28.32
Fl	trace
Limonite	.60
	99.72

Accompanying the wavellite and frequently upon the same specimen were observed nodular, light clay-like forms; sometimes, too, very dark nodules. Some of these revealed no definite radiating structure, while in others this was quite prominent; yet all trace of the white needles of wavellite had completely disappeared. In several instances these nodules were larger than a pigeon's egg. To learn their composition, specimens of both light and dark varieties were analysed. Light variety: sp. gr. 2.5.

H_2O	19.37 per cent.
SiO_2	32.42
Al_2O_3	23.19
Fe_2O_3	3.82
P_2O_5	19.19
CaO	1.00
MgO	.47
	99.46

Dark variety, sp. gr. 2.40. Analysis:

H_2O	26.29 per cent.
SiO_2	6.52
Al_2O_3	29.37
Fe_2O_3	15.61
P_2O_5	22.52
	100.31

5. *Corundum.*

This mineral, which we announced (Am. Phil. Soc. March 17, 1882) as occurring near Shimersville, Upper Milford Twp., has since been discovered there in exceedingly fine crystals; color grayish and red. In many the star is very distinct. The specimens are but slightly altered. The brilliant black crystals noticed upon almost all specimens from here have been found to be menaccanite. Dr. Genth (Am. Phil. Soc. Proceedings, Aug. 18, 1882) has published an account of the black spinel found here, which is unquestionably an alteration of the corundum. Very recently several students of this laboratory discovered fine specimens of it. An analysis of the Shimersville corundum gave the following:

SiO_2	3.28 per cent.
H_2O	1.37
Al_2O_3	85.75
Fe_2O_3	4.26
TiO_2	2.74
MgO	trace
CaO	1.99
Sp. gravity, 3.898.	99.39

6. *Tourmaline.*

Mr. Benj. Sadtler, Jr., of this laboratory, while searching for corundum at Shimersville, picked up a piece of feldspathic rock, often found here, in which were imbedded three or four large and quite perfect, black crystals of tourmaline. Want of time prevents giving an analysis of the same.

Dr. Henry K. Hartzell, of Allentown, also presented us with a hornblendic rock in which were beautiful brown tourmaline crystals, found near what is known as the Bethlehem Iron Co.'s mine on the Lehigh Mt., and not more than 1¼ miles northwest of Shimersville. A qualitative examination for identification is all that was made.

On the mountain, two miles south of Allentown, occurs a vein consisting of a brownish-black mineral, which in appearance reminds one greatly of allanite, but the incomplete analysis given below would indicate otherwise, and probably mark it as another occurrence of tourmaline. Its surface in many places is covered by a reddish colored mineral as yet unexamined. The dip of the vein is about 66°. The analysis as far as made is:

Loss upon ignition,	2.19 per cent.
SiO_2	39.41
Al_2O_3	19.46
Fe_2O_3	8.44
FeO	7.00
CaO	3.49
MgO	2.14
B_2O_3	9.00
Alkalies,	undetermined

7. *Garnet.*

At Mohr's magnetite mine in Upper Milford Twp., one-quarter mile from Shimersville, were found rather fine dark-red colored, imperfect dodecahedral crystals of this mineral. They occur in quartz and a granular limestone. The sp. gr. of well-selected material was 4.03, and an analysis of the same gave:

SiO_2	35.92 per cent.
Al_2O_3	19.18
Fe_2O_3	4.92
FeO	29.47
MnO	4.80
CaO	2.38
MgO	3.70
	100.37

Directly south of the above locality upon the land of Mr. Yeakel, quite a large bed of garnet in very minute dark-red crystals has been discovered. It occurs with magnetite.

Near Hosensack Station in Lower Milford Twp., on the Perkiomen R. R., exists a second variety of garnet, found by Mr. E. F. Krauss, '84, in perfect dodecahedral forms of olive color—occasionally the red variety is observed—in a matrix of feldspathic rock. Specular iron ore often accompanies the garnet. The rocks in this region, lying in the most chaotic condition, appear filled with garnets, mostly in well-defined moderately translucent forms. An analysis of the yellow variety gave:

SiO_2	35.25 per cent.
Fe_2O_3	32.17
FeO	.92
CaO	30.80
MgO	trace
	99.14

The specific gravity determined in two specimens was 5.05–5.27.

8. *Stilbite.*

This mineral was first found in Lehigh county, by Mr. E. F. Krauss, upon a limestone in the orchard of Mr. Jacob Schell, near Hosensack station. The specimens are in the form of large globular radiating concretions. Sp. gravity, 2.21.

Analysis.

SiO_2	55.31 per cent.
Al_2O_3	14.88
Na_2O	1.66
H_2O	18.47
	99.32

9. *Pyrolusite.*

At various times miners have reported this mineral as occurring in Lehigh county, but only of late have finely crystallised specimens of it been observed. The crystals are usually seen upon the inside of limonite nodules, frequently covering their entire inner surface. Those in our possession are from the Lehigh mountain south of Allentown, near the village of Mountainville:

SiO_2	9.93 per cent.
Fe_2O_3	4.21
Al_2O_3	trace
MnO_2	82.66
Mn_3O_4	3.13
	99.93

10. *Chloropal.*

A little west of the preceding locality are rather extensive iron mines. Over the entire mountain-top holes are observed (dug, evidently, in search of ore), and about these in the debris several students of this laboratory detected pieces of a yellowish-green colored mineral, so soft as to be readily impressed by the fingernail. Before the blow-pipe the material, although infusible, gradually assumed a black color and became magnetic; gave strong iron reaction and the silica skeleton. In a closed tube it yielded much water. Since the finding of the above specimens frequent visits have been made to this locality. On a recent trip, while examining some of the larger and deeper excavations, large pieces of the above mineral were noticed about six feet below the surface and overlying the iron deposit. The mineral varies somewhat in color from an olive to greenish-yellow. A number of analyses of the material brought in from time to time by various parties have been made, the results agreeing quite well and pointing to the mineral chloropal. The sp. gr. was found to be 2.033.

Analyses.

	1. Yellow.	2. Dark Yellow.	3. Greenish Yellow.
H_2O	19.61	19.79	18.65
SiO_2	40.20	40.81	42.31
Fe_2O_3	39.52	39.30	38.18
FeO	.40	...	trace
P_2O_5	trace	...	...
MgO	"	...	...
K_2O	"	...	...
	99.53	99.90	99.14

4. Yellowish Green.		5. Yellowish Green.	6. Light Yellow.
H_2O	20.79	20.45	19.09
SiO_2	41.16	41.41	42.79
Fe_2O_3	30.79	35.35	39.19
FeO	.21	...	...
Al_2O_3	2.05	3.04	...
K_2O[1]	4.54	...	...
	99.54	100.25	101.05

7. Brownish Yellow.		8. Same as 7.	9. As 7 and 8.
H_2O	19.27	19.31	19.31
SiO_2	42.37	41.35	41.13
Fe_2O_3	38.17	39.09	38.97
FeO	trace	...	...
P_2O_5	"	...	trace
MgO	"	...	"
	99.83	99.75	99.41

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[1] This is the only instance where so much alkali was observed.

	10. Brown Variety.	11. Yellowish Brown.
H_2O	17.71	19.36
SiO_2	43.54	43.00
Fe_2O_3	39.52	37.50
	100.77	99.86

The mineral decomposes completely with hydrochloric acid. In all cases the specimens under examination were carefully freed of any adhering ferric oxide, and tested for ferrous oxide, phosphoric acid, calcium and magnesium oxides, and the alkalies. No trace of crystallisation is present. The mineral is earthy in appearance, smooth to the touch, and may be polished by friction.

Some specimens, almost white in color, have been found; one of these gave the following quantitative results:

H_2O	17.65 per cent.
SiO_2	44.52
Fe_2O_3	11.04
Al_2O_3	25.95
MgO	trace
K_2O	.94
	100.10

We would here return thanks to our friends and students, Messrs. Benj. Sadtler, Jr., S. C. Schmucker and Ira Wise, for the care and willingness with which they have aided in the execution of the above and other chemical analyses.

Muhlenberg College, *June* 28*th*, 1883.

SOME MINERALS FROM BERKS COUNTY, PA.

By D. B. Brunner and Edgar F. Smith.

1. *Stilbite.*

At Wheatfield mines we found this mineral in radiating, fibrous, pearly-white masses upon a trap rock, together with exceedingly beautiful yellow-colored crystals of calcite. Specific gravity 2.2. An analysis gave:

H_2O	19.42 per cent.
SiO_2	57.49
Al_2O_3	13.03
CaO	8.06
MgO	trace
Na_2O	1.36
	99.36

We have also observed stilbite upon a Fritz Island rock in company with mesolite, but not in sufficient quantity to permit of an accurate analysis.

2. *Deweylite.*

In whitish and brownish resinous coatings upon aragonite and together with serpentine at Ruth's mine. Specific gravity 2.3. Analyses of two different specimens afforded us the following:

	A.	B.
H_2O	19.49 per cent.	19.03 per cent.
SiO_2	45.65	42.34
Fe_2O_3	0.20	1.39
MgO	34.38	36.77
CaO	trace	trace
	99.69	99.53

3. *Vesuvianite.*

At Fritz Island there has been for some time found a yellow-colored mineral in limestone, which upon examination gave about the composition of garnet, and was pronounced such until last fall, when we were successful in discovering finely crystallised specimens of the same and now know it to be vesuvianite. Our specimens are yellow in color, and exhibit forms consisting of tetragonal prisms with pyramids.

4. *Titanite.*

This mineral we have observed in clove-brown colored crystals in magnetite from a mine close to Huff's Church, Hereford Township. Our examination of the same, owing to scarcity of material, was limited to qualitative tests.

BRUCITE.

BY DR. J. SCHOENFELD AND EDGAR F. SMITH.

We have specimens of this mineral from two new localities in this State. The first place of interest where we have discovered it in fine large masses together with limestone and in distinct crystalline forms upon a dolomitic rock, is Fritz Island, near Reading. An analysis of a specimen from this locality gave:

MgO	66.78 per cent.
Fe_2O_3	.44
H_2O	32.52
	99.74

The second point at which it occurs, although not so abundantly as at the preceding place, is in a limestone quarry, about two miles south of Sinking Spring, Spring Township. This quarry was long operated for magnetic ore, but is now exhausted. The brucite exists in thin, colorless laminae in seams intersecting the limestone rock, much of which is rich in magnesia. On specimens of the dolomitic rock from this place we lately noticed fine silky white fibres, which to qualitative tests revealed the presence of much water, carbon dioxide and magnesia, indicating by these and physical appearance the mineral hydromagnesite. An analysis of the brucite resulted as follows:

MgO	66.19 per cent.
CaO	1.68
Fe_2O_3	1.24
H_2O	31.05
	100.16

Contributions from the Sheffield Laboratory of Yale College.

XVI.—ON SOME REDUCTIONS WITH ZINC AND AMMONIA. (SECOND PAPER.)

By W. G. Mixter.

Paraazoacetanilide.

It was stated in the footnote to the article (this Journal, **5**, 1) on reductions with zinc and ammonia, that azoacetanilide had been obtained. In the experiments there described on the reduction of nitracetanilide, the filtrate from the azoxyacetanilide was exposed for some time to the reducing action of zinc and ammonia, to make sure that no nitracetanilide remained in the solution. The results obtained since show that paraphenylenediamine was formed. If the reduction is stopped after the azoxyacetanilide ceases to separate from the solution in which it is formed, the alcoholic filtrate from the azoxy body leaves a residue on evaporation that contains azoacetanilide and considerable phenylenediamine. The diamine may be dissolved out with highly diluted hydrochloric acid; the undissolved portion, after thorough washing with water, is nearly pure azoacetanilide. It may be purified by dissolving in boiling alcohol and separating the hair-like crystals which form on cooling. Analysis *a* was made with substance obtained from evaporating the filtrate from the crystals, and *b* and *c* were of fibrous crystals of two different preparations. The drying was at 100° C.

a. 0.405 gram yielded 0.9655 gram of CO_2 and 0.2135 gram of H_2O. 0.4015 gram yielded 58.6 cc. of N at 2.4° C. and 766 mm. pressure.

b. 0.4144 gram yielded 0.9861 gram of CO_2 and 0.2083 gram of H_2O. 0.4161 gram yielded 63 cc. of N at 3.2° C. and 766 mm. pressure.

c. 0.3372 gram yielded 0.8005 gram of CO_2 and 0.1678 gram of H_2O. 0.3145 gram yielded 48.45 cc. of N at 4° C. and 750 mm. pressure.

Calculated for $C_{16}H_{16}N_4O_2$.		*a*	*b*	*c*
C	64.86	65.01	64.89	64.74
H	5.41	5.85	5.59	5.53
N	18.92	18.40	18.96	18.82

The azoacetanilide $\begin{array}{c} C_6H_4NHC_2H_3ON \\ \parallel \\ C_6H_4NHC_2H_3ON \end{array}$ is a para compound since it is derived from paranitracetanilide and converted into paraphenylenediamine by dissolving in strong hydrochloric acid, then adding tin. The azoacetanilide is evidently formed by the removal of one atom of oxygen from azoxyacetanilide, which is the first product of the reduction of the nitracetanilide. In one experiment azoxyacetanilide was dissolved in boiling alcohol and zinc and ammonia and platinum chloride were added. The solution was warmed from time to time until on cooling no azoxyacetanilide separated. After standing a day the solution was evaporated, and the residue after treatment with dilute acid was found to be azoacetanilide. Paraazoacetanilide melts at 281–2° C., has the color of gold, is insoluble in water, and is more soluble in alcohol than azoxyacetanilide.

Paraazoaniline.

Paraazoacetanilide dissolves in hot concentrated hydrochloric acid, both acetyl groups being replaced by hydrogen, with formation of a hydrochloride, which remains as a black mass after the solution has been evaporated on a water-bath. From the aqueous solution of the hydrochloride the base was precipitated with ammonia and was washed with water and dried at 100° C. Analyses I and II show the composition of this precipitate. The same compound was also formed by the saponification of azoacetanilide, which was obtained by reducing pure azoxyacetanilide as already described. Analyses III and IV show its composition.

I. 0.3158 gram yielded 0.7833 gram of CO_2 and 0.1621 gram of H_2O.

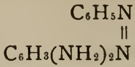
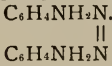
II. 0.2176 gram yielded 46.2 cc. of N at 4° C. and 763 mm. pressure.

III. 0.3555 gram yielded 0.8805 gram of CO_2 and 0.1838 gram of H_2O.

IV. 0.2053 gram yielded 43.2 cc. of N at 4° C. and 760 mm. pressure.

	Calculated for					
	$C_{12}H_{14}N_4$	$C_{12}H_{12}N_4$.	I.	II.	III.	IV.
C	67.29	67.93	67.64		67.55	
H	6.54	5.66	5.70		5.74	
N	26.17	26.41		26.39		26.05

The results correspond best with $C_{12}H_{12}N_4$.

Diamidohydrazobenzene, $C_{12}H_{14}N_4$, melts at 145° C.[1] Chrysoidine, $C_{12}H_{12}N_4$,[2] melts at 110° C., and forms the salt $C_{12}H_{12}N_4HCl$. Hofmann suggests the formula  $\begin{array}{c}C_6H_5N\\ \|\\ C_6H_3(NH_2)_2N\end{array}$ for chrysoidine, since it yields with nascent hydrogen aniline, and according to Griess triamidobenzene. The substance analysed melts at 235–240° C. and appears to form the hydrochloride $C_{12}H_{12}N_4.2HCl$. A weighed quantity of the substance was evaporated with hydrochloric acid, and the increase in weight corresponded with that required by the addition of two molecules of hydrochloric acid. Nascent hydrogen converts the new compound into paraphenylenediamine, an evidence that each benzene group contains one NH_2 group as represented by the formula  $\begin{array}{c}C_6H_4NH_2N.\\ \|\\ C_6H_4NH_2N\end{array}$ The name paraazoaniline which indicates this constitution is proposed. The writer has been unable to find any description of an azoaniline. Haarhaus[3] attempted to make diamidoazobenzene, *i. e.* azoaniline by reducing paranitraniline with sodium, but obtained diamidohydrazobenzene. Platinum chloride precipitates in a concentrated aqueous solution of the azoaniline hydrochloride, a salt which is somewhat soluble in water and very soluble in alcohol. Three preparations of the salt, dried at 100° C., yielded respectively 28.14, 28.53 and 27.80 per cent. of platinum. Theory requires 31.2 per cent. of platinum in $C_{12}H_{12}N_4H_2PtCl_6$ and 23.6 per cent. in $(C_{12}H_{12}N_4)_2H_2PtCl_6$. The quantity of platinum salt obtained was too small for complete analysis. Azoaniline has a dark yellow color, is slightly soluble in water and very soluble in alcohol, and its solutions have considerable coloring power. The solutions of its salts are red.

Paraazoxybenzanilide.

Mr. A. W. Robert, a student in this laboratory, has prepared the paraazoxybenzanilide by the method employed in making the metaazoxybenzanilide.[4] Pure paranitracetanilide was made and converted into paranitraniline. The nitraniline was heated with benzoyl chloride, and the paranitrobenzanilide formed was thoroughly washed with hot water and then recrystallised from boiling alcohol. It melted at 199° C. The following is the analysis of the azoxybenzanilide:

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[1] Lermontow, Berichte der deutschen chemischen Gesellschaft, **5**, 232.

[2] Hofmann, *Ibid.* **10**, 214, 390.

[3] Annalen der Chem. u. Pharm. **135**, 162.

[4] This Journal, **5**, 5.

I. 0.3607 gram yielded 0.9417 gram of CO_2 and 0.1519 gram of H_2O.

II. 0.316 gram yielded 33.4 cc. of N at 10° C. and 765 mm. pressure.

III. 0.2123 gram yielded 23.1 cc. of N at 14° C. and 762 mm. pressure.

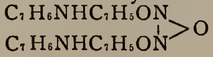
	Calculated for $C_{20}H_{20}N_4O_3$.	I.	II.	III.
C	71.56	71.23		
H	4.58	4.67		
N	12.85		12.92	13.04

The paraazoxybenzanilide melts at 310°, has a light yellow color, and is insoluble in alcohol and water. It dissolves readily in strong alcoholic potash, which converts it, on boiling, into paraazoxyaniline.

The alcoholic filtrate from the azoxybenzanilide was evaporated to dryness, and the residue was treated with boiling water and filtered hot. The portion insoluble in water was recrystallised from alcohol and analysed. The results indicated a mixture containing much unreduced nitrobenzanilide. The azobenzanilide looked for was not found. The hot aqueous solution yielded, on cooling, pearly crystals, which gave 13.11 per cent. of nitrogen and a platinum salt with 22.62 per cent. of platinum, results which indicate an impure amidobenzanilide. Theory requires 13.3 per cent. of nitrogen in the pure substance and 23.77 per cent. of platinum in its platinum salt. The substance melted at 110° C. Hübner states the melting point of paraamidobenzanilide at 128° C.[1]

Azoxybenztoluide.

Nitrotoluidine, melting point 77.5° C., was treated with benzoyl chloride, and the nitrobenztoluide, after washing with water, was dissolved in boiling alcohol and reduced with zinc and ammonia. The substance which separated from the solution was washed with alcohol, shaken with dilute hydrochloric acid, and finally washed with water, and dried at 100° C. The analysis shows that the compound is azoxybenztoluide



$$\left.\begin{matrix} C_7H_6NHC_7H_5ON \\ C_7H_6NHC_7H_5ON \end{matrix}\right> O$$

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[1] Annalen der Chemie, **208**, 295.

I. 0.427 gram yielded 42 cc. of N at 10° C. and 762.4 mm. pressure.

II. 0.4515 gram yielded 1.189 gram of CO_2 and 0.2166 gram of H_2O.

III. 0.3554 gram yielded 1.0148 gram of CO_2 and 0.1844 gram of H_2O.

	Calculated for $C_{28}H_{24}N_4O_3$.	I.	II.	III.
C	72.41		71.82	71.81
H	5.17		5.33	5.31
N	12.07	11.96		

Azoxybenztoluide melts at 290° C., has a light yellow tint, and is insoluble in water and alcohol.

Attempts to replace the benzoyl group by hydrogen have failed to yield azoxytoluidine, which Buckney has described.[1] Oil of vitriol at 100° and hydrochloric acid at 180° were tried.

The azoacetanilide and azoaniline complete the analogy indicated in the former paper[2] between the reduction products of nitrobenzene and those of paranitracetanilide, with the exception that no hydrazobenzene or benzidine analogue has as yet been obtained. The metaoxybenzanilide is the only meta compound of the series made thus far in the investigation. Experiments with impure orthonitracetanilide yielded only negative results. Perhaps orthonitrobenzanilide would give an azoxy body because of the greater insolubility of azoxybenzoyl compounds in alcohol. The results thus far obtained indicate that the hydrogen from zinc in ammoniacal solutions does not differ essentially from nascent hydrogen from other sources. The action of zinc and ammonia is less violent than that of zinc and acids, and is apparently better adapted to the formation of azo compounds. Zinc and ammonia do not separate the acetyl and benzoyl groups as would the fixed alkali in case sodium amalgam or caustic potash is used. Modifications of the method employed by the writer may perhaps be advantageously adopted. The presence of considerable ammonium chloride increases the evolution of hydrogen from zinc in solutions containing ammonia, and perhaps sodium amalgam may replace zinc with advantage in solutions containing sufficient ammonium salt so that sodium hydroxide cannot exist in the solution.

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 1452.

[2] This Journal, **5**, 7.

A CONVENIENT TEMPERATURE REGULATOR.

BY W. T. RICHMOND.

Notwithstanding that various forms of electrical temperature regulators have from time to time made their appearance, the following form of apparatus, devised and used with success by the writer in the laboratory of the Northern Transcontinental Survey, will, it is hoped, be found useful.

The apparatus may be said to consist essentially of three parts: A glass bulb *A*, a U tube *B* (Fig. I), and an apparatus *C* (Figs. I and II) by means of which the gas is turned off and on.

The glass bulb *A* is very conveniently made by drawing out the neck of a flask before the blowpipe, and fusing a glass tube of such a diameter that it will easily fit in the end of the U tube to the outdrawn neck. A larger piece of tubing is then put over the joint and plaster of Paris poured between. When the plaster sets the joint will be much strengthened. The U tube *B* (Fig. I) has a T joint at *a*, to the top of which is cemented a screw top, by means of which the regulator may be set at any temperature by leaving the top unscrewed until the required temperature is reached, at which degree the top is to be screwed down tight on the washer. In the middle of the U tube is a piece of platinum wire *b*, fused in the glass, so that the mercury which the tube contains will always be in contact with it. The wire is connected with a screw-cup *c*, which diminishes the danger of breakage. At the left-hand extremity of the tube is a screw-top *d* and screw-cup *e*. The screw-top *d* is to be tightly screwed down on the washer when the regulator is to be used for any great length of time, as by this means the barometric variations are without effect on the mercurial column. For ordinary use the top may be left unscrewed. A platinum wire *f*, having metallic connection with the screw-cup *e*, passes down the tube to within a short distance of the mercury. The wire is fused in a small piece of tubing, as shown in the figure. By this means the air space of the U tube is diminished, and consequently the liability of the mercurial column being influenced by the outside temperature. The screw-cup *e* is, of course, for the battery wire.

The part of the apparatus *C* (Figs. I and II) consists of an electro-magnet *D* and a funnel *E*. The armature of the electro-magnet has affixed to it a brass rod *g*, and is connected at its extremity with the rubber diaphragm *h*, which covers the mouth of the funnel, being held in place by a rubber band. A spring is seen connected with the armature, which serves to bring it back to its original position after the electro-magnet ceases to act. The glass funnel *E* is about four inches in diameter. Through the side of the funnel is drilled a small hole of such a size that the piece of rubber tubing *i* fits gas-tight. To the centre of the rubber diaphragm *h* is attached a small T tube, as represented in Fig. II, the T of which is attached to the rubber tubing *i* conveying the gas. Through the neck of the funnel passes a brass rod having a thread cut on it and working in a nut *j*, which rests at the junction of the funnel and neck. The upper part of the rod carries a cup *k*, in which is put a little mercury, or what is perhaps better than the cup, a rubber stopper. It will be obvious that the screw-working rod acts only as an aid in adjusting the apparatus when it is first put up.

One part of the T tube is attached to the rubber diaphragm *h*, while the other, through which the gas passes when not shut down, is just a little above the mercury cup or stopper. The whole T works on the flexible joint *i*. The T tube has a small hole in it through which just enough gas passes to keep the Argand burner *F* lighted when the diaphragm *h* is pressed down. The gas passes into the apparatus through the glass tube *b*, as indicated by the arrow, out through the neck of the funnel, whence rubber tubing takes it to the burner *F*.

The apparatus is set up and worked as follows: The glass bulb *A* (Fig. I) is placed in the air-bath *G*, and the smaller piece of tubing *m* is pushed into the end of the U tube *B*, where it is cemented by means of plumber's cement. The gas is let into the apparatus, the Argand burner is lighted, the screw-top *a* is opened; the nut-working rod is screwed up until the mercurial cup or rubber stopper is near enough to the orifice of the T tube delivering the gas to cause the flame to fall when the diaphragm is slightly depressed. One wire of the battery is connected with the screw-cup *e*, the other being placed in connection with screw-cup *n*. A piece of copper wire connects *o* and *c*, *n* and *o* being the ends of the electro-magnet wire. When the proper temperature is reached, as indicated by the thermometer in the air-bath, the screw-top *a* is screwed down tight. The residual air in *A* con-

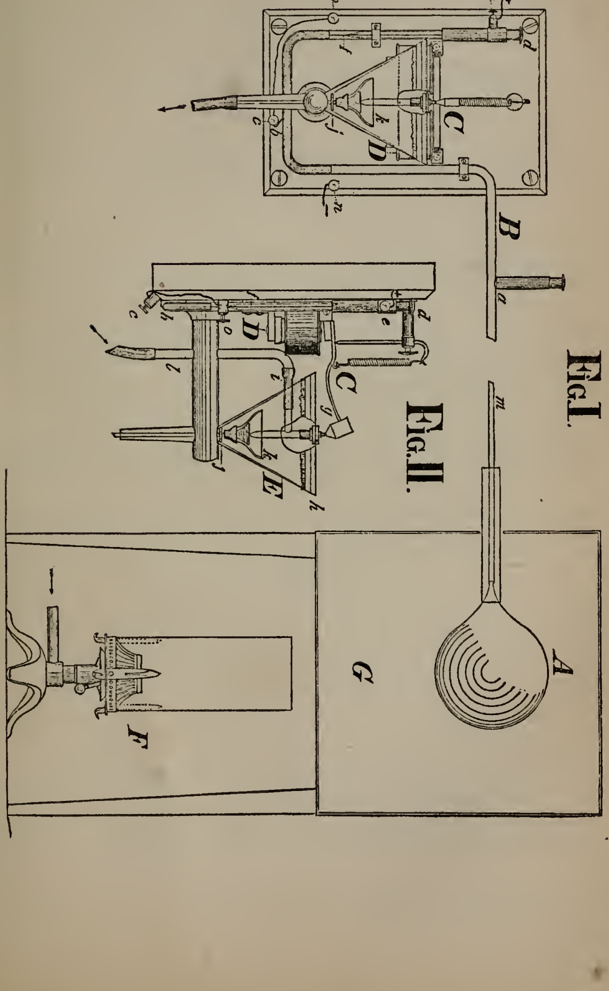

Fig. I.

Fig. II.

tinuing to expand, pushes the mercury in the U tube until it comes in contact with the platinum wire *f*. At this instant the electric circuit is completed, the electro-magnet attracts the armature, the diaphragm *h* is depressed, the flow of gas is almost entirely cut off, the flame of the burner falls, the temperature sinks, the air in the bulb contracts, the mercurial column breaks contact with *f*, the spring attached to the armature draws the diaphragm back to its original position, the free flow of gas again takes place, and the apparatus is again in its former condition, the alternations of course taking place as often as contact is made and broken by the mercurial column and *f*.

I find plumber's cement to be well adapted for cementing the screw tops to the U tube.

The diaphragm covering the mouth of the funnel may be made of rubber or other flexible gas-tight material.

The mercury used in the U tube should be perfectly *clean*.

The apparatus made as above described will, I find, keep the temperature constant to within ½°–1°, provided the flame of the burner is not so large as to overheat the air-bath before the air-bulb has time to respond.

In conclusion I wish to thank Mr. Whitfield, Assistant Chemist to the Northern Transcontinental Survey, who kindly prepared the drawings from which the above cut was made.

THE VOLUMETRIC DETERMINATION OF MANGANESE.[1]

By J. B. Mackintosh.

In a recent paper read before the Institute on this subject, Mr. G. C. Stone advances the theory that the precipitate obtained in Williams's volumetric process,[2] by treating the boiling nitric acid solution of a manganese salt with potassic chlorate, is not pure

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[1] Read at the Roanoke Meeting of the American Institute of Mining Engineers.

[2] Transactions of the American Institute of Mining Engineers, **10**, 100.

MnO_2, but approximates more closely to the composition $10MnO_2 + MnO$.

As the value of the process and the accuracy of our results would depend on whether this was the fact or not, it has seemed to me, and to my associates, Messrs. Beebe and Colby, that it would be of importance to ascertain the composition of this precipitate, and to that end the following series of experiments has been undertaken.

These experiments have all been based on the considerations:

1. That potassic permanganate has an oxidising power equivalent to five atoms of oxygen for every two of manganese:

$$K_2Mn_2O_8 = K_2O.2MnO.O_5.$$

2. That the same amount of manganese in the state of binoxide, has an oxidising power equivalent to two atoms of oxygen:

$$2MnO_2 = 2MnO.O_2.$$

If, then, we take a solution of permanganate of unknown strength, and reduce it to binoxide, the oxidising power of the binoxide formed will be equal to that of two-fifths the quantity of the permanganate solution originally taken. While, if the precipitate obtained should not be binoxide, but an indefinite or definite mixture of bin- and mon- oxides, then, from its equivalent oxidising power, we can calculate its composition.

The analyses were conducted in the following manner. The amount of permanganate taken was decomposed with hydrochloric acid, and concentrated to expel the excess of water. Sufficient excess of nitric acid was now added, and the solution was boiled until all the hydrochloric acid was destroyed. The manganese was then precipitated by potassic chlorate; and, after standing some time to cool—a precaution which we consider of importance—the precipitate was filtered out through asbestos, washed with nitric acid, and then with water, and when perfectly clean was treated with a volume of oxalic acid, whose equivalent in permanganate was known, a few cubic centimeters of sulphuric acid being also added. The excess of oxalic acid was then estimated by permanganate, and the difference between this amount and the equivalent of the whole amount of oxalic taken gave the oxidising power of the precipitate.

To save multiplication of figures we will only give the results obtained:

$K_2Mn_2O_8$ used.	Oxidising power of precipitate in terms of $K_2Mn_2O_8$.	Theoretical for. MnO_2.	Apparent per cent. of theoretical.	Corrected per cent. for burette error.
cc.	cc.	cc.		
45	17.80	18	98.89	99.37
35	13.93	14	99.50	100.07
25	9.90	10	99.00	99.86
15	5.96	6	99.33	100.67
			Average true per cent.,	99.99

The precipitation in the above results was affected by successive alternate additions of potassic chlorate and nitric acid, until no further formation of yellow fumes was observed. Shortly after first employing the method, we noticed that the reaction was seldom complete when potassic chlorate was added during one period only, and that if, after the apparent completion of the reaction, as marked by the explosive cessation of yellow fumes, more nitric acid was added, and then a fresh portion of potassic chlorate, the yellow fumes would reappear, again to disappear with the characteristic puff. On this account it is necessary in employing this method, to add alternate amounts of nitric acid and potassic chlorate, until no further effect is produced; and, if this precaution is not observed, the results will almost invariably be low.

The next series of experiments was made to illustrate this point, and to determine the amount of error which would be incurred by exactly following the directions given by Messrs. Ford[1] and Williams in their respective papers, namely, by adding potassic chlorate during one period only and boiling till the apparent cessation of the reaction. The results obtained were as follows:

$K_2Mn_2O_8$ used.	Oxidising power of precipitate in terms of $K_2Mn_2O_8$.	Theoretical for. MnO_2.	Apparent per cent. of theoretical.	Corrected per cent. for burette error.
cc.	cc.	cc.		
40	15.55	16	97.20	97.82
45	17.70	18	98.33	98.92
60	23.37	24	97.40	98.04

Showing an error of from one to two per cent.

The following determinations were made about last February, but no particular record of the details of the manipulation were preserved:

25	9.93	10	99.30	98.34
50	19.73	20	98.65	99.07

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[1] Transactions of the American Institute of Mining Engineers, 9, 397.

It is evident from inspection of these results, that the first set approach very nearly to the theoretical figure for MnO_2, the average of the four happening to be 99.99 per cent. This close agreement with theory must, however, be considered as largely accidental, as the variation in the separate determinations is quite large. In a process of this kind we must consider that the experimental errors are relatively large; indeed, larger than in the actual application of the method to analysis. These experimental errors, doubtless, balance each other to a large extent by averaging several results, as in the present instance; but we can hardly expect to get such close average results every time.

The burette was calibrated for each analysis by weighing the amount of water delivered corresponding to the various volumes used, and making proportional corrections.

Now, if the composition of the precipitate had been $10MnO_2 + MnO$, as claimed by Mr. Stone, the oxidising power found should have averaged 90.91 per cent. of the theoretical figure for MnO_2, instead of that which we have actually found; so that the difference is far too great to admit of any doubt as to the true composition of the precipitate. We may safely conclude, then, that the precipitate obtained in this process, when due regard is paid to the precautions which we have indicated, is MnO_2, and not an indefinite or definite mixture of oxides, that the process is reasonably accurate, and that any estimation based upon the theory that the precipitate is not MnO_2 is of no value, because it is founded on false premises, and therefore can never be true save by accident.

REVIEWS AND REPORTS.

THOMSEN'S "THERMOCHEMICAL RESEARCHES."[1]

Three years ago Berthelot's important treatise on thermochemistry appeared, and now the literature of the subject is still further enriched and the work of students facilitated by the publication in book form of Thomsen's numerous and valuable researches, which in main part have appeared in various scientific journals from time to time during a long series of years. The author announces that the work is to consist of four volumes, entitled as follows: I. Neutralisation; II. Metalloids; III. The Metals; IV. Organic Compounds. The greater part of the material of the first three volumes has already been published in separate papers. Considerable additions of new material and revisions and redeterminations in the old have, however, been made.

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[1] Thermochemischen Untersuchungen. Von Julius Thomsen. Leipzig, Barth, 1882.

The fourth volume will be essentially new, only one or two brief publications having been made of the author's researches in the thermal phenomena of organic compounds. And the nature of these communications leads one to anticipate that volume IV will be of the greatest interest. At the time of writing only volumes I and II are in print.

One cannot but be impressed by even the first half of the work with the enormous amount of patient and skilled labor involved in these extended researches, and the whole may justly be termed colossal. In his first volume Thomsen gives but a brief exposition of the general principles upon which the science of thermochemistry is based. Indeed, judging from the two volumes at present in print, we should say that for the systematic development of the science of thermochemistry, or, more broadly speaking, of chemical mechanics based upon thermochemistry, of its general principles and of its relations to other branches of physics, Berthelot's treatise is superior. For the precise and accurate determination of the fundamental numerical data, which must, of course, furnish the basis of the system, the comparison might perhaps be more in favor of Thomsen's work. Fortunate it certainly is for the science that the parallel labors of these two eminent investigators furnish results which control and, in general, confirm each other.

Volume I contains the results of about 1100 calorimetric determinations, involving some 600 chemical reactions. The greater part of these pertain to the thermal phenomena of neutralisation proper, involving the detailed study of the combination of some 45 different acids, organic and inorganic, with sodic hydrate; and on the other hand of 42 bases, organic and inorganic, with sulphuric, hydrochloric, nitric and some other acids. In these experiments acid and base are present not only in equivalent quantities, but the effect of acid and base in excess upon the phenomena is studied, and conclusions drawn therefrom with reference to basicity of acid and to the existence of acid and basic salts in solution. In this way the calorimeter in many cases confirms the accepted notions upon the subject, and in some solves questions which purely chemical methods fail to answer. In addition to these elementary data the author treats, more or less briefly, some points of more immediate and general interest, viz. the thermal phenomena of single, double and partial decomposition, and the so-called "avidity" of acids, which is determined in 17 cases; the rôle of water in aqueous solution, the specific heat of solutions, and the variations of heat disturbance with temperature.

A valuable feature of the work is that the actual experimental data used in the calculation of final results are given in detail. For example, take a single determination of the heat evolved in neutralising sulphuric acid with sodic hydrate, or as Thomsen expresses it, Na_2OAq,SO_3Aq. We find given :

Temperature of air $= T = 18.3°$
" " NaHO Sol. $= t_a = 18.545°$
" " H_2SO_4 " $= t_b = 18.468°$
" on mixing $= t_c = 22.801°$
Heat disturbance in calorimeter $= r = 3921$
Fraction of molecular wt. used $= s = \frac{1}{8}$
Heat disturbance for molecular reaction $= R = 31368$ cal.

The general formula used by Thomsen to calculate the value of r is

$$r = (t_c - t_a)a + (t_c - t_b)(b + p) + q\tfrac{a}{450}, \qquad (1)$$

in which a is the weight of water in first solution, b of second, p the calorific equivalent in H_2O of calorimeter and its appurtenances, and q a constant correction for difference in the reading of thermometers used; the other letters having the significance indicated above. In the experiment cited $a = b = 450$ grams, $p = 13$ grams, $q = 0$. In general the solutions of acid and base contain 200 H_2O for one equivalent of substance.

It will be seen that the above formula (1) is based upon the assumption that the calorific equivalent of the resulting salt solution is equal to the sum of the calorific equivalents of its constituent acid and base solutions, and that the calorific equivalent of each of the latter is equal to the weight of water therein contained.

As this assumption is only approximately true, the formula based upon it gives only approximate results. The exact formula, omitting the correction for thermometer readings, would be the following :

$$r = (t_c - t_m)(m + p) \qquad (2)$$

in which $t_c =$ observed temperature after mixing.
$t_m =$ " " of constituent solutions before mixing, supposing them to be at the same temperature.
$m =$ calorific equiv. of resulting salt solution.
$p =$ " " of calorimeter and belongings.

If the constituent solutions are not at the same temperature before mixing, t_m would be given by the formula,

$$t_m = \frac{a\,t_a + (b + p)t_b}{a + (b + p)}$$

in which a and b are calorific equiv. of base and acid solutions, and t_a and t_b their respective temperatures. This may be simplified to $t_m = \frac{t_a + t_b}{2}$ without introducing appreciable error in the usual conditions of experimentation. The error introduced by the assumption which Thomsen uses for the calculation of the amount of heat disturbance is probably small also, when the solutions have the degree of dilution generally employed, viz. 200 H_2O for one equiv. of substance. How small the error is only a special determination of the specific heat of the given solutions can show. For example: the reaction $Na_2O\ 200H_2O + H_2Cl_2\ 200H_2O = Na_2Cl_2\ 401H_2O$ gives by formula (1) the value 3438 for r. Calculated by formula (2), using Thomsen's determination of the specific heat of $Na_2Cl_2\ 400H_2O$, $r = 3408$, a difference of .87 per cent. In most cases the error is probably less than this, but it is evident that it may be safely neglected only when the solutions are considerably diluted and the change in temperature small. In these conditions the actual specific heat being unknown, Berthelot assumes for the purpose of approximate calculation that the calorific equivalent of 1 cc. of the primitive solution is equal to that of 1 gram of H_2O. Thus the volume of $HCl + 100H_2O = 1818.5$ cc. (temperature 18°), of $NaHO + 100H_2O = 1795.9$ cc.; their sum 3614.4 is the cal. equiv., by Berthelot's assumption, of $NaCl + 201H_2O$. By Thomsen's hypothesis this quantity is 3600. On the assumption that the specific heat of the solutions is 1 (which is often made) this value is 3676.5. The experimental determination of it by Thomsen gives 3596.

The author gives a short chapter to the subject of the variation of heat disturbance with temperature. With a knowledge of the specific heat of the solutions in question, the amount of this variation for one degree of temperature may be calculated by the formula $\varphi = \frac{R_T - R_t}{T - t} = q_a + q_b + q_c$, in which R_T and R_t represent the heat disturbance for the temperatures T and t; q_a and q_b represent the quantities of heat required to raise the component solutions from t to T, and q_c the quantity required to raise the resultant solution from t to T. This formula is derived directly from the second principle of thermochemistry, called by Berthelot the principle of "Initial and Final State."

Thomsen gives a few instances of the experimental determination of this variation of heat disturbance between the temperatures of 9 and 25°, and compares these values with those calculated by the above formula and the specific heats determined by himself. The reactions are those involved in the formation of Na_2SO_4, $(NH_4)_2SO_4$, NaCl and NH_4Cl in the usual conditions. The results are respectively:

ϕ by direct experiment.	ϕ by formula.
— 27 cal.	— 29 cal.
+ 69	+ 65
— 43	— 45
+ 2.6	— 3

In spite of the considerable accordance between these series of differences, we doubt very much whether the quantities are far enough removed from the limits of experimental error to be much relied upon.

One of the most interesting points considered in Thomsen's first volume is the so-called avidity of acids or partial decomposition in aqueous solution. When two given acids in equivalent quantities are brought in contact with one equivalent of base in aqueous solution, there is in certain cases a division of the base between the acids. The ratio of the fractions of the base thus divided is, according to Thomsen's definition, the relative avidity of the acids.

For example, when 1 equiv. of sulphuric acid and 1 equiv. of nitric acid are in presence of 1 equiv. of sodic hydrate, it is found that $\frac{1}{3}$ of the base is in combination with the first and $\frac{2}{3}$ with the second acid. Making the avidity of hydrochloric acid unity, that of sulphuric acid .50. To determine the quantity of base combined with each acid is a difficult problem, since all the substances remain in solution. Thomsen succeeds in solving it by calorimetric methods. Without giving the details of the process we may state that to determine the avidity of H_2SO_4 and HNO_3, the heat disturbance of the following reactions must be measured:

1. Neutralisation of H_2SO_4 by NaHO.
2. " " HNO_3 " "
3. Decomposition of Na_2SO_4 by HNO_3.
4. " " $NaNO_3$ by H_2SO_4.
5. Sulphate + H_2SO_4 in varying quantity.
6. Nitrate + HNO_3 " "
7. $H_2SO_4 + HNO_3$.

The author finds that the relative avidity varies with the base employed, but is apparently independent of the degree of dilution and of the temperature, or at least the variation is so small as to escape measurement by his methods. He finds no relation apparent between relative avidity and heat of neutralisation or the basicity of the acid. Nor do his results accord with Berthollet's theory of partial decomposition. They do, however, afford a satisfactory experimental test of the correctness of the theory of Guldberg and Waage. Berthollet's theory for the division of a base between two acids is formulated by Thomsen as follows: let b and b' represent the fractions of the base in combination with the acids; M and M' their respective masses, and x and x' their "affinities." Then $\frac{b}{b'} = \frac{Mx}{M'x'}$; but $M = \frac{aA}{g}$ and $M' = \frac{a'A'}{g}$ in which A and A' are the equivalents of the acids, and a and a' the number of equivalents present; hence $\frac{b}{b'} = \frac{aAx}{a'A'x'}$. "Affinity" is defined by Berthollet as the reciprocal of equivalent; hence $\frac{x}{x'} = \frac{A'}{A}$ and the formula becomes $\frac{b}{b'} = \frac{a}{a'}$. Further, if there are B equivalents of base present, $b + b' = B$. From these two equations $b = \frac{aB}{a + a'}$ and $b' = \frac{a'B}{a + a'}$. This formula is evidently not in accordance with fact, since b and b' have by it the same value for any couple of acids. If we make $a = a' = B = 1$, then $b = b' = \frac{1}{2}$, which is certainly not true for many couples.

If instead of $\frac{b}{b'} = \frac{a}{a'}$ we use $\frac{b}{b'} = \frac{m}{m'} \cdot \frac{a}{a'}$, in which $\frac{m}{m'}$ is constant for the same system of base and acids, it will be seen that when $a = a'$, $\frac{b}{b'} = \frac{m}{m'}$, or in other words that $\frac{m}{m'}$ is the ratio of Thomsen's so-called avidities. From this modified formula we obtain $b = \frac{amB}{am + a'm'}$ and $b' = \frac{a'm'B}{am + a'm'}$. The values of b and b' given by these formulas are compared with the values given by experiment when the system is made up of Na, H_2SO_4, and HNO_3. Here $\frac{m}{m'} = \frac{1}{2}$ as determined calorimetrically by Thomsen, or in other words, the avidity of HNO_3 is twice that of H_2SO_4. In the conditions of the experiment $a = B = 1$ and a' is variable. The following table gives the results:

a'	Exp.	Theo.
$\frac{1}{8}$	— 904 cal.	—1456
$\frac{1}{4}$	—1616	—2626
$\frac{1}{2}$	—2584	—3010
1	—3504	—3548
2	—4052	—3824
3	—4100	—3918

The third column gives the heat disturbance calculated for the values of b and b' given by the above formula, while the second column gives the values obtained by experiment. It will be seen that the theory does not accord with fact. If we turn to the theory of Guldberg and Waage, we find better success. This theory as applicable to the cases experimented upon may be formulated as follows: Let P and Q represent two substances which by double decomposition produce R and S; a, b, c, d, the number of equiv. of each present before reaction; x the number of equivalents decomposed. Then after the reaction the system becomes $(a - x)P + (b - x)Q + (c + x)R + (d + x)S$. Let K represent the force by which $P + Q$ tend to become R and S, and $1/K'$ the force of the opposite reaction, $R + S = P + Q$. Now by this theory $K(a - x)(b - x) = 1/K'(c + x)(d + x)$. Putting for convenience $KK' = n^2$ and finding the value of x gives

$$x = \frac{n^2(a+b)+c+d-\sqrt{[n^2(a+b)+c+d]^2-4(n^2-1)(n^2ab-cd)}}{2(n^2-1)}$$

To apply this formula the value of n must be determined. This is done by measuring x experimentally with given values for a, b, c, and d. In the case under consideration, viz. the reaction $Na_2SO_4 + 2HNO_3$, when $a = b = 1$ and $c = d = 0$, $x = \frac{2}{3}$ determined calorimetrically by Thomsen. Substituting in formula gives

$$x = \frac{n}{n+1} = \frac{2}{3}, \text{ whence } n = 2.$$

Substituting this value of n in the formula gives

$$x = \frac{4(a+b)+c+d - \sqrt{[4(a+b)+c+d]^2 - 12(4ab - cd)}}{6}$$

From this x may be calculated for all values of a, b, c and d. In the following table are compared the values given by this theory and those given by experiment; the system being Na, H_2SO_4, HNO_3:

$$a = 1$$
$$b = c = 0$$

b	x	Exp.	Theo.
$\frac{1}{8}$	0.121	904 cal.	924 cal.
$\frac{1}{4}$	0.232	1616	1656
$\frac{1}{2}$	0.423	2584	2662
1	0.667	3504	3546
2	0.845	4052	3948
3	0.903	4100	4038

Similarly the results of four other series of experiments are compared by the author with the results deduced from the theory, and in no case is the difference more than .3 per cent. of the heat of neutralisation. The agreement becomes more remarkable when we consider that the calculated experimental values involve the determination of at least three different quantities.

If in the equation $K(a-x)(b-x) = 1/K'(c+x)(d+x)$, we make $a = b = 1$ and $c = d = 0$ and $KK' = n^2$, then by reducing $n = x/1-x$. But x and $1-x$ are the fractions of the base in combination with the two acids respectively when 1 equiv. of each substance is present. Hence n becomes the relative avidity of the two acids for the given base, according to Thomsen's definition.

Another point in Vol. I. may be mentioned as of general interest, viz. the author's conclusion that, for the same acid, the true heats of neutralisation in solution are the same for the alkalies, the alkaline earths and the magnesium bases, Mg, Mn, Ni, Co, Fe, Cd, Zn and Cu; and that where there is an apparent difference, it is due to difference in the heat of solution; and, further, that in solution, as in the gaseous form, we have a condition which permits the comparison of the physical properties of substances in their simplest relations.

A. V. E. Young.

NOTES.

Contributions to the Chemistry of the Cerite Metals.

The figures hitherto obtained in the determinations of the atomic weight of didymium vary between the limits 142 and 147.2. The most recent determinations are those of Cleve (147.2) and Brauner (146.58)[1]. As the difference of more than five units between the above numbers is greater than could be attributed to mere experimental errors, B. BRAUNER "undertook experiments to decide which of the numbers represents, or more nearly approaches, the true atomic weight of didymium, and to ascertain whether pure didymium is a homogeneous body, or whether it can be split up into heterogeneous constituents, as has proved to be the case with several metals of the rare earth group." Didymium oxide was, for this purpose, purified in three ways and the atomic weight determined. It was found to be 145.42, the determinations differing only between the limits 145.53 and 145.31. This number differs very sensibly from those found by Cleve, viz. $Di = 147.2$, and from those obtained in the author's former experiments, viz. $Di = 146.58$, and this difference cannot be attributed to mere experimental errors. On the contrary, the true reason of this discrepancy may, as it seems, be looked for in the circumstance that an element of a higher atomic weight and of a less basic nature than didymium was eliminated from the original oxide, by precipitating the small traces of cerium present, together with a portion of the didymium with ammonia.

A careful examination showed that the element of a higher atomic weight is samarium. The highest atomic weight obtained was 149.4. The substance giving this result was found to contain 25.2 per cent. of didymium, so that the atomic weight of samarium deduced from these data is $Sm = 150.7$. The atomic weight of the purest didymium prepared is $Di = 145.4$, which number may be assumed to represent, as nearly as possible, the true atomic weight of didymium.—(*Journal of the* (*London*) *Chemical Society*, 1883, 278.)

A new Substance in Benzene from Coal Tar.

In a recent number of this Journal[2] attention was called to some observations made by VICTOR MEYER, which led to the conclusion that there is some difference between the benzene obtained from coal tar and that from benzoic acid. The author has continued his experiments, and has succeeded in isolating from coal tar benzene a peculiar substance containing sulphur, which he calls thiophene. It is this substance which gives to benzene the power to unite with isatin, phenylglyoxylic acid, benzoyl cyanide, etc., in the presence of sulphuric acid. The fact that coal tar benzene is turned brown by concentrated sulphuric acid, while pure benzene is not affected in this way, is also due to the presence of thiophene in the former.

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[1] When $O = 16$ and $S = 32.07$.

[2] Vol. **3**, 481.

The isolation of thiophene was effected in a chemical factory. 250 litres of the purest commercial benzene were shaken for four hours with 25 litres of concentrated sulphuric acid. After the removal of the layer of benzene, the black acid mass was diluted with water and the lead salt of the sulphonic acid prepared. The quantity of salt obtained in this way—mainly the lead salt of the new sulphonic acid together with some benzenesulphonate—amounted to 16 kilograms. From the lead salt the new body may be obtained easily in large quantity. It is decomposed by means of hydrogen sulphide and then subjected to dry distillation, or it is distilled with hydrochloric acid, or with ammonium chloride. In either way there is obtained a light volatile oil which boils for the greater part at 84°. This product may be obtained in large quantity from the lead salt. From each kilogram of the salt there were obtained about 80 grams of the new body. It is a light, limpid, very mobile oil, with a slight odor suggesting that of benzene. It does not solidify in a mixture of ice and salt. It dissolves in concentrated sulphuric acid, the solution being of a deep brown color. When the oil is treated with bromine it yields a product of the formula $C_4H_2Br_2S$, which in odor and other general properties closely resembles bibrombenzene. The monobrom derivative, the sulphonic acid, the sulphochloride, sulphamide and the carbonic acid of the new body also resemble the corresponding derivatives of benzene. Thus apparently an extensive new field is opened, the cultivation of which will yield a large number of interesting bodies, the properties of which will be similar to those of the corresponding derivatives of benzene. Their constitution will also be similar, only instead of from benzene they will be derived from a mother substance containing sulphur. For the latter the author proposes the name *thiophene*. In addition to the properties above stated, the following may be mentioned: It is stable towards alkalies and even the alkali metals. It remains unchanged when boiled for hours over sodium. Nitric acid oxidises it with violent action.

All commercial benzene contains thiophene. An estimation of sulphur in a specimen of the purest coal tar benzene indicated the presence of about 0.5 per cent.

It would be premature to attempt to determine the constitution of the new body at present. The analogy between the formulas of thiophene, C_4H_4S, and furfuran, C_4H_4O, is suggestive, and, further, the striking similarity between the derivatives of thiophene and benzene. The author suggests that thiophene may be benzene in which two CH groups are replaced by an atom of sulphur.—(*Berichte der deutschen chemischen Gesellschaft*, **16**, 1465.)

The Preparation of Aluminium.

According to a statement in the *Bulletin de la Société de l'industrie minérale*, **2**, 451, Salindres is at present the only factory in which aluminium is manufactured. The quantity manufactured is about 2400 kilograms annually. The sodium is prepared by igniting sodium carbonate with charcoal and a little lime to facilitate the distillation, the requisite chlorides of aluminium and sodium by distilling a mixture of alumina, charcoal and sodium chloride in a current of chlorine. The distilled double salt is then melted together with sodium and some cryolite to serve as a flux.

Recently the statement has been current in a number of journals that material improvements have been made in the manufacture of aluminium at the *Aluminium Crown Metal Works*, in Hollywood, which are under the direction of J. Webster. It is said that a ton of the metal costs now only 2000 marks ($500), while it formerly cost 20,000 marks ($5000). According to the latest statement on the subject, the new method consists in igniting bauxite with sodium carbonate, decomposing the sodium aluminate with carbon dioxide, heating the separated alumina with charcoal in a current of chlorine, and melting with sodium and cryolite the double chloride of sodium and aluminium thus obtained.

It does not appear probable that by this method, which is essentially an old one, a kilogram of aluminium can be made for two marks, or indeed even for 20 marks.

J. Webster, in Solihul (Austrian Patent, Sept. 28th, 1882), describes the following *method for the preparation of alumina for the purpose of manufacturing aluminium.* 3 parts of alum are mixed with 1 part of coal pitch, and the mixture heated to 200 to 260°. In about three hours the pasty mass is spread upon a stone floor, and, after it has become cool, it is broken in pieces. Hydrochloric acid of 20 to 25 per cent. is poured upon these pieces placed in piles, which are from time to time turned over. When the evolution of sulphuretted hydrogen has stopped, charcoal powder or lamp black to the extent of about 5 per cent. and enough of water to make a thick mass are added. The mass is thoroughly broken up and mixed in a mill, and then worked into balls of about 0.5 kilogram each. These are bored through to facilitate drying, and heated in a drying chamber at first to 40°, then in a furnace at 95 to 150°. The balls are now kept for three hours at a low red heat in retorts, while a mixture of two parts water vapor and one part air is passed through, so that sulphur and charcoal are converted into sulphur dioxide and carbon dioxide and thus escape. The current of gases carries over some potassium sulphate, ferric sulphate and alumina, and is hence brought into clay condensers. After the substances mentioned have been driven off, the dry residue is removed from the retort and cooled, again placed in the mill and ground to a fine powder, which consists of aluminium oxide and potassium sulphate. This powder is treated with about seven times its weight of water, then boiled in a pan or boiler by means of steam for about an hour, and allowed to stand until cool. The solution containing potassium sulphate is run off, and evaporated to dryness; the alumina is washed out and dried.

J. Morris, of Uddington, near Glasgow (German Patent, No. 22150, August 30, 1882), claims to obtain *aluminium by treating an intimate mixture of alumina and charcoal with carbon dioxide.* For this purpose a solution of aluminium chloride is mixed with powdered wood, charcoal and lamp black, then evaporated, until it forms a viscous mass, which is shaped into balls. During the evaporation hydrochloric acid is given off. The residue consists of alumina intimately mixed with charcoal. The balls are dried, then treated with steam in appropriate vessels for the purpose of driving off all the chlorine, care being taken to keep the temperature so high that the steam is not condensed. Now the temperature is raised, so that in the dark the tubes are seen to be at low red, and dry carbon dioxide then passed through. This is said to be reduced by the charcoal to carbon monoxide, which now, as affirmed by Morris, reduces the alumina to aluminium.

Although the quantity of the escaping carbon monoxide is in general a good indication of the progress of the reduction, it is nevertheless advisable not to continue the heating of the tubes or vessels until the evolution of this gas has ceased or even nearly ceased, as, in consequence of slight differences in the consistence of the balls, some of them give up all their carbon sooner than the others. The treatment of the balls with carbon dioxide for the purpose of the reduction lasts about 30 hours, when the substances are mixed in the proportions of 5 parts carbon to 4 parts alumina.

As Morris states, further, the metal appears as a porous, spongy mass. It is freed from the residual alumina and particles of charcoal by fusion and mechanical treatment and then poured into molds.—(*Dingler's Polytechnisches Journal*, **249**, 86.)

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—AMERICAN.

BLOXAM, C. L. Chemistry, inorganic and organic, with experiments. 5th Ed. Philadelphia: Blakiston.

BROWN, W. L. Manual of assaying gold, silver, copper, and lead ores. Chicago: Jansen, McClurg & Co.

GRIFFIN, LA ROY F. Lecture notes in chemistry: a syllabus compiled principally from the manuals of Miller and of Roscoe and Schorlemmer. Philadelphia: Sower, Potts & Co.

HOFFMANN, F., and POWER, F. B. A manual of chemical analysis as applied to the examination of medicinal chemicals and their preparations. 3d Ed., entirely rewritten and enlarged. Phila.: H. C. Lea's Sons & Co.

MITCHELL, C. Practitioner's guide to urinalysis. Chicago: Gross & Delbridge.

PINNER, A. Introduction to organic chemistry. Translated and revised by P. T. Austen. N. Y.: Wiley.

SHERRERD, J. M. Iron analysis record. Troy: Young.

SOUTHWICK, A. P. Question book of chemistry. Syracuse: Bardeen.

STODDARD, J. T. An outline of qualitative analysis for beginners. Northampton: Gazette Printing Office.

II.—ENGLISH.

FENTON, H. J. H. Notes on qualitative analysis, concise and explanatory. London: Cambridge Warehouse.

FRANKLAND, P. F. Agricultural chemical analysis. London: Macmillan.

MORGAN, C. L. Water: its teachings in chemistry, physics, and physiography. London: Stamford.

RIDSDALE, C. H. Chemical percentage tables and laboratory calculations. London: Crosby & Lockwood.

III.—FRENCH.

BOUANT, E. Cours de physique et de chimie, rédigé conformément au programme des écoles normales primaires d'instituteurs. Paris: Delalain.

CLAPARÉDE, A. Quelques nouvelles kétones aromatiques obtenue par condensation moléculaire. Genève.

DELAURIER, E. Essai d'une théorie générale supérieure de philosophie naturelle et de thermochimie, avec une nouvelle nomenclature binaire notative pour la chimie minérale et organique. Fasc. I. Paris: imp. Lahure.

DOCUMENTS sur les falsifications des matières alimentaires et sur les travaux du laboratoire municipal. Paris: Masson.

FABRE, E. Étude sur les eaux minérales de Caprem. Paris: Davy.

GIRARDIN, J. Leçons de chimie élémentaire appliquée aux arts industriels. Tom. III. Chimie organique. Paris: Masson.

KLEIN, D. Sur les acides borotungstiques. Paris: Gauthier-Villars.

LEPLAY, H. Chimie théorique et pratique des industries du sucre. T. I. Paris: Baudoin.

MORELLE, E. Recherches chimiques sur la bergenite. Lille: Danel.

PELIGOT, E. Traité de chimie analytique appliquée à l'agriculture. Paris: Masson.

PELLET, H., et SEUGIER, G. La fabrication du sucre. Tom. I. Paris: Pellet.

PISANI, F., et DERVELL, P. La chimie du laboratoire. Paris: Baillière.

POIRÉ, P. Leçons de chimie. Paris: Delagrave.

SCHUTZENBERGER, P. Traité de chimie générale, comprenant les principales applications aux sciences biologiques et aux arts industriels. Tome III. Paris: Hachette.

THOMAS, A. Manuel de l'alcoömetrie. Lille: Michelet.

IV.—ITALIAN.

SBRIZIOLO, M. Trattato di chimica analitica qualitativa ed quantitativa. Napoli: Eschera.

SBRIZIOLO, M. Trattato di chimica generale inorganica ed organica. Napoli.

V.—SCANDINAVIAN.

SCHMELCK, L. Chemistry of the Norwegian North-Atlantic Expedition. 1. On the solid matter in sea water. 2. On oceanic deposits. Christiania.

VI.—GERMAN.

BEILSTEIN, F. Handbuch der organischen Chemie. Leipzig: Voss.

BERGHAUS, A. Das Glycerin, seine Gewinnung und Verwendung in der Industrie. Berlin: Pohl.

ELSNER, F. Recepte für Pharmacie und chemische Grossindustrie. Halle: Knapp.

FLÜCKIGER, F. A. Die Chinarinden. In pharmakognostischer Hinsicht dargestellt. Berlin.

GROSHANS, J. A. Ein neues Gesetz analog zu dem Gesetz von Avogadro. Deutsch von F. Roth. Leipzig: Barth.

HOFMANN, A. W. Chemische Erinnerungen aus der Berliner Vergangenheit. Zwei akademische Vorträge. Berlin.

HAUSSKNECHT, O. Lehrbuch der Chemie und chemischen Technologie. Hamburg.

KAYSER, H. Lehrbuch der Spectralanalyse. Berlin: Springer.

KOLBE, H. Lehrbuch der organischen Chemie. Braunschweig.

KÜNSTLE, G. Kohlenstoff-Skizzen. Ein organisch-chemisches Hohes Lied. München.

LEDEBUR, A. Die Metallverarbeitung auf chemisch-physikalischem Wege. Braunschweig: Vieweg.

LIPPMANN, E. O. v. Die Zuckerarten und ihre Derivate. Vom Vereine für die Rübenzucker-Industrie des Deutschen Reiches mit dem ersten Preise gekrönte Monographie. Braunschweig.

LOEW, O., und BOKORNY, T. Die chemische Kraftquelle im lebenden Protoplasma. Muenchen.

Medicus, L. Kurze Anleitung zur Massanalyse. Im Anschlusse an die "Kurze Anleitung zur qualitativen Analyse." Mit specieller Berücksichtigung der Vorschriften der Pharmakopöe bearbeitet. Tübingen.

Meyer, L., und Seubert, K. Atomgewichte der Elemente aus den Originalzahlen neu berechnet. Leipzig: Breitkopf und Härtel.

Palm, R. Grundriss der qualitativen und quantitativen chemischen Analyse, nebst einer General-Tabelle der wichtigsten Pflanzen-Alkaloide und einer Spectral-Tafel. Leipzig.

Raspe, Fr. Heilquellen-Analysen für normale Verhältnisse und zur Mineralwasserfabrikation, berechnet auf zehntausend Theile. 1 Liefrg. Dresden.

Rieth. Volumetrische Analyse. Hamburg.

Schaedler, C. Die Technologie der Fette und Oele des Thier- und Pflanzenreichs. Berlin.

Schmid, A. E. v. Leitfaden für den Unterricht in ausgewählten Kapiteln der chemischen Technologie. Graz.

Schultz, G. Die Chemie des Steinkohlentheers mit besonderer Berücksichtigung der künstlichen organischen Farbstoffe. Braunschweig.

Schwanert, H. Lehrbuch der pharmaceutischen Chemie. In 3 Bdn. Braunschweig: Schwetschke und Sohn.

Schwackhöfer, F. Lehrbuch der landwirthschaftlich-chemischen Technologie mit besonderer Berücksichtigung der österreichischen Verhältnisse. Zum Gebrauche an landwirthschaftlichen u. technischen Lehranstalten, sowie für Landwirthe, Industrielle, Steuerbeamte, etc.

Winkler, Cl. Die Maassanalyse nach neuem titrimetrischem System. Kurzgefasste Anleitung zur Erlernung der Titrirmethode. Der chemischen Anschauung der Neuzeit gemäss bearbeitet. Freiberg.

Zaengerle, M. Grundriss der Chemie und Mineralogie. Nach den neuesten Ansichten der Wissenschaft für den Unterricht an Mittelschulen, besonders Gewerbe-, Handels- und Realschulen bearbeitet. I Theil. Anorganische Chemie und Mineralogie. Braunschweig.

UNIVERSITY PUBLICATIONS.

Jena.

James, W. Ueber die Derivate des Aethylen chlorobromids; insbesondere über das Aethylen chlorsulfocyanat und seine Reactionen.

Knorre, G. v. Beiträge zur Kenntniss der Wolframverbindungen.

Scheid, B. Beiträge zur Kenntniss des Benzo-chinons.

F. W. C.

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ON THE USE OF MERCURY THERMOMETERS WITH PARTICULAR REFERENCE TO THE DETERMINATION OF MELTING AND BOILING POINTS.

By J. M. Crafts.

The progress made during the last twenty years in the preparation and purification of chemical substances has not been followed by a corresponding improvement in the methods which serve to determine some of their physical properties, and this is particularly true of determinations involving the measure of temperature.

The methods used for the graduation of thermometers are often unreliable, the modes of reading them give varying results, and the ordinary tables of corrections contain errors much greater than those which it is intended to correct.

A series of experiments[1] was undertaken with a view to remedying some of these defects by processes which can be easily carried out in a chemical laboratory, and they were extended to an examination of the best methods of manufacturing nearly accurate thermometers, after it was discovered that the principal defects can be remedied by means easily within the reach of a careful instrument-maker. In fact, the methods of preparation and of graduation of thermometers for higher temperatures, which will be proposed, are similar to the processes now in use for pointing the scale between zero and 100°; and it is hoped that they will insure nearly as great accuracy for the temperatures between 100° and 360° as is now obtained with normal thermometers between zero and 100°.

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[1] Some of the experiments described in this paper have been published in the Comptes Rendus, **91**, 291, 370, 413, and 574; **94**, 1299, and **95**, 836 and 910. The theoretical considerations of the articles in the Comptes Rendus are here omitted, and a greater development is given to the practical directions concerning laboratory operations. The table of corrections for thermometers with a limited scale has been added.

The different sources of error in the kind of thermometric observations that we are considering will be examined in detail.

Mercury Thermometers.—The Calibration.

The standard thermometers made at the observatory at Kew, and those of M. Baudin, of Paris, are calibrated before graduation in order that the stem may be divided into parts of equal capacities, and a subsequent calibration made with the best apparatus shows residual errors of 0.015° to 0.04°, when the scale is divided in tenths of a degree. The process of correction of the errors of calibration and graduation attains an exactitude 0.002°.[1]

Thermometers made with extraordinary care, and divided into 500 parts between zero and 100 degrees, or into 360 degrees for the complete scale, are found to have a mean error not greater than one-third of a division.

The thermometers ordinarily used in chemical laboratories are far from being equally exact; for instance, 19 French and German thermometers were found to have differences of 0.1° to 0.5° in the length of contiguous sections of 25 degrees. If the tube is regularly conical these differences are cumulative; thus an error of 3.6 degrees at 230° was found in calibrating a thermometer of this kind (the value of the degree between zero and 100° was taken as unity).

Most frequently the variations in the length of a column have sometimes a plus, sometimes a minus sign, but these errors do not usually cancel each other, and it is rare to find ordinary thermometers which do not require at several parts of their scale corrections for errors of calibration amounting to a large fraction of a degree; hence for accurate work the thermometer should be calibrated according to one of the methods described in physical text books.

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[1] M. Pernet, of the International Bureau of Weights and Measures at Sèvres, has had the kindness to furnish the details regarding the calibration of standard thermometers.

It is impossible by the ordinary processes to calibrate the thermometers intended for use at high temperatures, when the tube contains air; but the following method gives a sufficiently exact calibration when the upper reservoir is large enough to contain at least $\frac{1}{10}$th of the mercury of the bulb. The bulb is heated until part of the mercury rises into the reservoir and there a globule is separated by a jerk, and by trial a sufficient quantity is detached to make a column of 20 to 30 degrees. The thermometer is allowed to cool in such a manner that this small column follows the mercury in the stem with an interval of 10 to 30 degrees, which space is necessarily filled with air. On account of the air it is impossible by the usual method to change at will the position of the separated column; it follows the main body of the mercury, but it may be fixed without great difficulty at the required points by heating the bulb to temperatures which must remain constant during each observation of the length of the small column. For this purpose a very simple thermostat is employed, consisting of a copper tube about 25 cm. long with the sides 3 mm. thick. The bulb of the thermometer is introduced into the tube, placed horizontally, where it is heated by conduction, and the temperature is regulated by placing the lamp under the tube at the requisite distance from the part containing the bulb of the thermometer. In this way it is easy to maintain a sufficiently constant temperature, because small movements of the main body of the mercury do not usually force the detached column to change its position.

The Value of the Degree.

The first accurate researches in thermometry were made in order to find suitable means of determining the two points which fix the value of the degree, and the necessary precautions for determining the freezing and boiling point are described in the physical text-books. It is important to use a good barometer, which does not require a notable correction for the capillary depression; and in order that the reduction of the mercury column to zero may be exact, the barometer should be sheltered from rapid changes of temperature. This may be conveniently effected as recommended by Professor Rowland, by wrapping the barometer with its thermometer in several folds of flannel. Instead of the boiling apparatus of Regnault, a glass flask with a long neck of at least 6 cm. diameter may be substituted without diminishing notably the accuracy of the determination. In all cases the bulb and the entire mercury column must be heated in the steam.

The thermometer may be inserted through a pin-hole pricked in a thin diaphragm of rubber, so that only a few tenths of a degree need be withdrawn from the steam in order to make an observation. Zinc or copper turnings are put in the water.

It is very important to follow an invariable order in observing the points 100° and zero. The 100° point is observed first, and it is indispensable to make the zero determination immediately afterwards. Instead of allowing the thermometer to cool in the vessel used for the boiling point of determination, it should be taken out quickly, while heated to 100°, and as soon as it has taken nearly the temperature of the air (this requires 5 to 7 minutes) it is plunged into snow which has been for a long time in contact with distilled water. When snow cannot be procured, it is best to substitute ice finely divided by planing it with an ordinary wood plane. This artificial snow may be placed in a cavity at least 5 cm. in diameter, made in a mass of pounded ice, filling a large vessel, which should be provided with means for draining off the water.[1]

Even with the best thermometers it is not common to find that exactly 100° of the scale are comprised between the temperature of steam at 760 mm. pressure (barometer reduced to zero) and the temperature of melting ice. The standard thermometers show divergences of several hundredths of a degree, and thermometers which are made for use in chemical laboratories have errors which are sometimes as high as zero, 0.8° in 100°, which would entail an error of 2.4° at 300°, since all the measures of temperature are divided by the value of the degrees established between 100° and zero.

It is necessary always to follow the method indicated, or at least an invariable matter in determining the value of an interval 100°–zero, since a variation of method may cause this quantity to vary 0.2° to 0.5°.[2]

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[1] In all exact determinations the snow should cover a considerable part of the scale, and instead of uncovering the zero at the moment of reading its position, it is preferable to bring this point before the smaller aperture of a conical glass tube, which is embedded in the snow, so that the divisions of the thermometer can be read by looking into the larger end. With this arrangement the scale can be conveniently observed with a telescope furnished with a micrometric eyepiece, the lighting is good, and the air of the tube being cooled to zero, the observation is not hindered by the moisture which is usually condensed on the stem of the thermometer in the ordinary method of making zero point determinations.

[2] The method here recommended has always been followed by certain experimentalists, and M. Baudin has employed for a long time a similar process for the graduation of his thermome-

Even when an invariable method is employed for the observations, important errors may proceed from another cause, which has hitherto escaped attention: the value of the degree itself usually varies each time that a change of position of the zero point occurs, and all the constants of the thermometer are changed in different proportions.

During the ordinary usage of a new thermometer at temperatures above 100° a gradual elevation of the zero point takes place, and the value of the degree changes at the same time. This movement has been followed with seven thermometers made at Paris, of crystal glass containing about 18 per cent. of oxide of lead; and during a series of experiments like those common in chemical laboratories, the following elevations of the zero point and augmentations of the interval 100° to zero were observed simultaneously. The movement was progressive during the whole series of experiments, but only the final variations are given in the table.

Nos. of thermometers	45	46	47	50	52	53	54
Rise of the zero point	2.11°	1.24°	1.36°	2.76°	2.38°	3.39°	2.40°
Increase of the interval 100°– 0°	0.14°	0.06°	0.05°	0.13°	0.10°	0.19°	0.07°

By inducing larger elevations of the zero point the corresponding changes in the interval 100° to zero can be better studied, because certain irregularities are then only of slight relative importance compared with the larger numbers which have to be considered.

The following series of experiments is well fitted to show the magnitude of these changes, and they were also undertaken particularly to test the point whether the changes produced at mod-

ters, but it is only lately that the rule can be considered as established among physicists to take as a point of departure of each measure of temperature the position of the zero point determined immediately after each observation. The best arguments in favor of this mode of proceeding have been given in the excellent memoir of Dr. Pernet, who has shown what confusion arises when the zero point is observed before the determination of temperature. In this last case it is necessary to take into consideration the changes which preceding operations have caused in the position of the zero point, and a minute study of the special qualities of the thermometer is required before the measures taken by different methods can be compared with each other. Dr. Pernet has calculated a series of corrections of this kind for temperature between zero and 100°, and the data will be given further on for making similar calculation in the case of higher temperatures, but only when the zero point at its maximum of elevation is to be dealt with. The observations of several authors lose all value as true measures of temperature from the absence of details regarding the method which they have employed. It is to be noticed that the graduation of instruments at the Kew observatory is still based upon the determination of the zero *before* that of the higher temperature.

erately high temperature were similar in character to those observed after heating to the highest temperatures to which the thermometer can be conveniently exposed.[1]

Nos. of thermometers	1	2	3	4	5
Rise of the zero point	23.0°	24.0°	26.0°	16.6°	11.0°
Increase of the interval 100°–0°	0.9	0.45	0.85	0.50	0.70

Nos. of thermometers	6	7	11	13	15
Rise of the zero point	15.8°	11.7°	9.9°	12.0°	13.7°
Increase of the interval 100°–0°	0.80	0.50	0.94	0.77	1.30

The thermometers Nos. 1, 2, 3, 4, 11, 13 and 15 were made of French crystal glass containing about 18 per cent. of oxide of lead. The Nos. 5, 6 and 7 were of German soda glass. The seven thermometers were heated eleven days at 355°. The Nos. 11, 13 and 15 were heated three years at 166°, 206° and 266°. It will be seen that similar effects are produced at these relatively lower temperatures and at the highest, and no known fact justifies the opinion of several authors that the phenomena which take place when glass is heated change their character at the different temperatures within the above range. Even at 100° by prolonged heating an augmentation equal to about 0.05° of the interval 100° to zero may be produced, while the position of the zero point is raised by some tenths of a degree.

Thus after any change in the position of the zero the interval of 100° to zero must be determined anew, and usually a new value for the degree will be found by which all the measures of temperature must be divided. But measures thus corrected will probably not stand in a simple relation with the old ones, and after each considerable change of the position of the zero point the thermometer should be again compared with the air thermometer throughout the whole length of its scale in order to establish a new series of corrections.

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[1] Dr. Pernet (Comptes Rendus **91**, 471) had stated his opinion that no variation of the interval of 100° to zero is produced when the heating takes place at temperatures not higher than 100°. According to my experiments a variation of the interval must always be looked for when the position of the zero point changes, and under certain conditions a constant relation may be observed between the amplitudes of these two movements. I have given (Comptes Rendus **91**, 574) an hypothesis which may serve as a guide to the study of this phenomenon, but I do not propose here to discuss theoretical views, nor to enter into the details of certain experiments which were suggested by them. In this paper it is intended only to discuss the side of the question which is practically more important: namely, the possibility of obviating this source of error. The means by which this result may be effected will be described in full. They consist in a preparatory treatment of the thermometer which serves to make the position of the zero stable within certain narrow limits, and at the same time the value of the degree becomes practically unalterable.

It will be thus seen that this phenomenon has a most disastrous influence upon the precision of thermometric measurements, and it is important to examine into the causes of these movements and to endeavor to find means to suppress them.

Depression of the Zero Point.

Let us consider the case of a thermometer which has been brought by special treatment to what may be called its normal condition at the ordinary temperature. This is effected by causing the disappearance of certain persistent and abnormal expansion of the glass by heating a very long time (several days at 355°) and by cooling very slowly (during several weeks). When such a thermometer is heated successively at a series of different temperatures, each higher than the last, and after each heating cooled immediately in the air and the zero point observed, a depression of zero is found to correspond with each successive heating at the increasing stages of temperature, and the extent of the depressions rises in a more rapid ratio than the temperatures of the heatings to which they correspond.

It is a well-known fact that the extent of the depression depends upon the manner in which the thermometer is cooled to the ordinary temperature; for example, after heating to 100°, if the thermometer, instead of cooling directly in the air for 5 to 7 minutes, is taken from the heating apparatus and plunged immediately into a series of baths regulated at 60°, 30°, etc., it can be brought to the temperature of melting ice in one or two minutes, and in this case the position of the zero is about 0.05° lower than in the first case. This process of rapid cooling by means of baths is employed by M. Baudin, and consequently the interval of 100° to zero on his thermometers is greater by 0.05° than it is found when determined by the method recommended in this paper.

If the thermometer is cooled as slowly as possible during twenty-four hours after having been heated to 100°, the position of the zero is about 0.15° higher than when it is cooled in the air, and the position of the zero point is raised about 0.15° still higher when the thermometer is cooled slowly and methodically during a period of several weeks. It is evident that each way of operating would give a different value for the degree.

The method which has been recommended above gives values for the interval 100° to zero which are constant to about one hundredth of a degree.

The first vertical column of the table contains the numbers designating six thermometers of which No. 5 is made of soda glass, the others are of crystal containing about 18 per cent. of oxide of lead. The remaining columns give the depressions corresponding with the temperatures to which the thermometers have been heated.

It is to be noted that the time required to produce a maximum depression varies with the temperature. At 60° it requires several days, at 100° a few hours, and at the highest temperature from ten to fifteen minutes. The position of the zero at the maximum of depression remains constant on successive heatings at the same temperature.

Table of Zero point Depressions.

Temperatures	40°	60°	80°	100°	160°
No. 1	0.00°	0.06°	0.19°	0.31°	0.74°
5	0.04	0.08	0.18	0.29	0.56
13	0.02	0.03	0.17	0.31	0.69
15	0.01	0.05	0.18	0.31	0.75
31	0.02	0.06	0.22	0.37	0.84
32	...	...	...	0.28	0.69

Temperatures	218°	260°	306°	355°
No. 1	1.12°	1.33°	1.63°	2.19°
5	0.76	0.91	1.14	1.51
13	0.87	1.09	1.30	2.15
15	0.97	1.12	1.40	2.05
31	1.15	1.46	1.77	...
32	0.98	1.21	1.56	2.06

This table may be used in the following manner to compare observations made by different methods. Suppose, for instance, that a temperature has been measured by the method which was chiefly used formerly, the zero point was first taken, and then a series of rising temperatures was observed, as for example 100°, 200° and 300°. The same observations referred to a zero point determined immediately after each one will give the measures 100.3°, 201.0° and 301.5°, if the depressions had been the same as the thermometer No. 1 in the table. All these last observations are to be divided by 1.003, which is the value of the degree in this case, and thus the second method would give 100°, 200.4° and 300.6° instead of 100°, 200° and 300°. The table of corrections to reduce the scale of mercury thermometers to that of a gas thermometer is founded on the assumption that the last method of observation has been employed; and consequently when any other method is used, additional corrections like those above must be applied, and the rate of the zero point depressions under the circumstances of the experiments must be known.

The preceding calculations are only applicable to the cases in which the zero point has completely returned to its normal position at the commencement of a series of experiments, and also the successive heatings must take place at increasing temperatures. Very often the depression of the zero produced by the preceding experiments still persists at the commencement of a new series, and in that case, instead of observing a depression on heating, a rise of the zero point is to be noticed, and a knowledge of the laws regulating the elevation of the zero is required to calculate its position in such an experiment. It will be seen that the relations between the measures made by different systems may become extremely complicated, and it is to avoid difficulties of this nature that an invariable method has been recommended, viz. that which takes for the point of departure of each measure the position of the zero determined immediately after each observation of temperature.

The Rise of the Zero Point.

After a depression of the zero point, if the thermometer is left at the ordinary temperature, the zero is found to gradually rise through a tendency to return to its original position,[1] and the study of such movements as may be produced by exposing a thermometer during a very long time to constant temperature gives the data for calculating the position of the zero point under all circumstances, and what is more important, the study of this question leads to the discovery of the means for preventing those variations of the constants of a thermometric scale which are fatal to the precision of all measurements. It is particularly from this point of view that we are interested in the subject, and only those details will be given which have a direct bearing upon improvements in the manufacture of thermometers.

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[1] I have followed this movement under varied conditions in order to ascertain if it is regular, *i. e.* if the experiments can be so arranged as to give identical results under conditions which appear to be similar. In more than 1000 observations the divergences which escape a control of this sort do not appear to exceed 0.02° to 0.03°, but it would be very difficult to find a general formula for a movement which not only depends upon the time but also upon the temperature, and it must also be remembered that the depressions whose disappearance constitutes the phenomenon to be observed are often due to successive heatings at various temperatures, and represent the accumulation of several different impulses.

Mr. Mills in a general formula for the rise of the zero point at the ordinary temperature appears to have taken into account no factor except the time.

If after a depression produced by heating a thermometer is heated at a lower temperature, the zero point tends to gradually return to the position which is normal for this last temperature. The complete return or rise of the zero is more rapid in proportion as the temperature which produced the depression is not far removed from that which brings about the rise. The time required for this movement is measured by hours at the highest temperatures and for small intervals (10° to 20°), and by days or months at lower temperatures (100° or the ordinary temperature). When the interval is very large a part of the depression produced at a high temperature is permanent at the lower temperature. Thus a thermometer heated at 355° may be left for an indefinite period at the ordinary temperature without showing a rise of the zero equal to more than one-half of the true depression, but this depression may be made to disappear entirely when the thermometer is heated methodically for several days at each of the temperatures 300°, 250°, 200°, and so forth, to the ordinary temperature.

When a new thermometer is heated during a week or ten days at 355° a very considerable rise of zero is noticed. In the case of soda glass the zero may rise 10° or 15°, and with crystal glass 15° to 26°. This movement is probably the return from a depressed position, like those which have been previously described, and it may be assumed that the depression of the zero or the abnormal expansion of the glass was produced during the operation of blowing the bulb of the thermometer, and that it has resulted from the rapid cooling of the glass while still soft. Moreover, as it has been seen that the depressions of the zero point produced at 355° or 300° persist at the ordinary temperature, so also this abnormal expansion produced at a red heat is permanent at low temperatures. And it is in accordance with the rule derived from the previous results that the abnormal expansion should disappear when the thermometer is heated to a temperature nearer to that which produced the expansion. Thus the extraordinary rise of the zero point which may be produced by heating to 355° or higher temperatures is probably almost entirely due to the same causes which induce the permanent elevation of the zero point at the ordinary temperature, and the effects which previous observers have attributed to the pressure of the atmosphere are really due to an interior transformation[1] of the glass, almost or quite independent of external pressure. Thus similar results are obtained with vacuous or air-filled thermometers, and the progress of the changes, which have to do almost exclusively with the duration of time and the temperature to which a thermometer of a given kind of glass is exposed, is entirely under control.

Let us examine the rapidity of the change at different temperatures. The rise of the zero point in a thermometer which is kept at the ordinary temperature becomes continually slower, and ceases to be appreciable after five or ten years. Thermometers have been observed for more than two centuries, and even after this great lapse of time the displacement of the zero is not more considerable. It usually attains about one-half a degree. In the same way the rise of the zero which is produced by heating to any fixed temperature tends to reach a limit, and the whole movement appears to be more rapidly completed the higher the temperature. On heating to 355°, after ten days, without having reached the limit, the thermometer may be considered as having become virtually stable, since the movement of the zero point has become so slow that no noticeable displacement is produced during any ordinary experiments of short duration, even when the heat is carried as high as the boiling point of mercury, and such a thermometer may be heated several days at 300° or 200°, or several months at 100°, or it may remain several years at the ordinary temperature without alteration to the effect produced at 355°. By this is meant that, although certain slight elevations take place at lower temperatures such as those which have been previously described, yet, whenever the thermometer is heated again to 355°, the zero point immediately returns to the position which it had after the first prolonged heating in boiling mercury. It may be concluded from what precedes that the extreme variations of the zero point to be observed with what has been called a stable thermometer, are comprised within limits of about 2° between the point of extreme depression for 355°, and a complete return to the higher position corresponding with the ordinary temperature, and the table of depressions gives the point within these limits to which the zero may be brought and permanently fixed by heating at any constant temperature.[1] Similar series of observations were made with exactly similar results when, instead of 355°, the highest limit of temperature was fixed at 300°, 260°, 200° or 100°.

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[1] Dr. Löwenberg (Berichte chem. Gesell. **10**, 472) supposes that the particles of glass after heating are in a state of tension produced by the slight conductibility of glass, which occasions a cooling or setting in successive layers, and that this abnormal tension may disappear in consequence of oft-repeated molecular movements.

I am unable to estimate the consequences which follow upon this manner of considering the phonomena, but the following experiment was suggested by M. Dufour's observations upon rapidly cooled glass drops. He found that these drops contain a vacuous cavity, and consequently that after the solidification of the outside layer the interior mass must solidify under a diminished tension. It occurred to me to examine whether the exterior layer of the bulb of a thermometer exercises mechanical pressure on the interior layers: the result was negative. A large thermometer, newly made, was left in hydrofluoric acid until about one-third of the thickness of the bulb was dissolved, and no considerable change in the position of the zero took place. Care was taken to open the stem before the experiment in order to guard against the effect of the pressure of the atmosphere upon the bulb, made thinner by the action of the hydrofluoric acid.

It will be seen that only thermometers that have thus been made stable can be used where the position of the zero is to be determined by calculation, and what is more important it is that only with such instruments is the value of the degree constant, and that with constant thermometers any table of corrections obtained by comparison with an air thermometer remains permanently applicable. It may be added that the curve of corrections for thermometers that have been so heated as to produce the largest displacement of their zero point does not vary in form from the curves of corrections to be applied to new thermometers to bring their scale into accordance with that of a gas thermometer. Five of the thermometers which were used in my experiments to compare the mercury with the hydrogen thermometer were subjected to a prolonged treatment at high temperatures, and the curve of average corrections obtained with these five instruments was found not to differ essentially from the average corrections determined from the other thermometers.

The Preparation of Thermometers.

The conclusions to which the preceding paragraphs lead may be summed up in a few general directions for rendering thermometers unchangeable. Those which are intended for the ordinary experiments between zero and 360° should be heated throughout the whole length of their stem for a week or 10 days in boiling mercury, and the graduation, the determination of 100° and zero points, and the calibration, should be made after this treatment; they then acquire a permanent value. When the scale only extends to some lower temperature, 200° or 100°, the time required for the preliminary treatment is proportionally longer. To prepare a standard thermometer for use at temperatures between zero and 100° it should be heated throughout its length for several weeks at 100°, or the process may be shortened by heating it in essence of turpentine at about 156° for four days and then for a week at 100°.

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[1] This statement must be taken in conjunction with what has been previously said concerning the persistency of depression for long intervals of temperature, and the appropriate means of making them disappear.

The thermometers must not in any case be subjected for a long time to the action of water, and all these operations can be most conveniently carried out with a metallic apparatus, which is similar to that described further on for fixing accurately certain temperatures, except that many of the precautions there recommended for avoiding slight variations may be omitted. A cylindrical vessel of copper or iron with an hermetically fitting cover communicates with the air by means of a tube, upon which is fixed a condenser, so that evaporation is prevented and the heating at a constant temperature may be prolonged for any length of time. The thermometers are placed in an interior tube closed at the bottom and fitted into the cover with a perfectly tight joint. All the joints are brazed when the apparatus is made of copper. They are fitted by grinding and sweating on when the apparatus is made of iron. These pieces of apparatus have been found most convenient for heating sealed tubes or for any laboratory work where a fixed temperature is required. By the use of several substances, boiling under varied pressures, any temperature can be maintained constant for days or months to within one-fifth degree. They require no attention to regulate temperature, they are quickly heated and cooled, and if the sides are properly protected by a non-conducting jacket they are much more economical of gas than any oil or air bath used for similar purposes. This mode of maintaining fixed temperatures, which was first studied by Regnault, cannot be too highly recommended for laboratory work.

A tight-fitting apparatus for boiling mercury is difficult to construct, and when it is only to be used to prepare "constant" thermometers for graduation (but not to graduate them), it suffices to use an iron tube closed by welding at the bottom, 5 or 6 cm. wide and one metre long, filled with mercury to a height of 5 cm. This lower portion is heated directly over the lamp. A non-conducting jacket protects a length above this of 60 cm., and the mercury condenses in the upper part of the tube, which is exposed to radiation. Or in case mercury fumes are to be feared, the upper end of the tube can be surrounded by a condenser. The thermometers are enclosed in a sealed glass tube. A similar form of apparatus has been found most convenient for boiling sulphur and other substances in Victor Meyer's vapor density determination.

Corrections to be applied to the results obtained with the Mercury Thermometer to bring them to the true temperature as measured by a Hydrogen Thermometer.

Each mercury thermometer has its individual scale requiring somewhat different corrections, but since the publication of Regnault's memoirs it has been customary to distinguish two categories of thermometers according as the glass is crystal containing oxide of lead or is ordinary glass. The columns A and B in the table below contain the corrections of Regnault for crystal glass from the manufactory of Choisy-le-Roy, containing 34 per cent. of oxide of lead, and for ordinary French glass.

Neither of these kinds of glass is now used to make thermometers. The crystal which is employed at Paris contains about 18 per cent. of oxide of lead; the German soda glass is free from lead, but it is much more fusible than ordinary French glass, hence a revision of these tables has become necessary. The column C of the table was obtained by experiments with 14 crystal glass thermometers made at Paris, and with a soda glass thermometer made at Bonn. To use the table the number of degrees centigrade is read off on the mercury thermometer, the position of the zero is determined immediately afterward, and the correction if necessary is made for its displacement; then the corrections of the table, observing their signs + or —, are added to the numbers of degrees thus obtained, and give the temperature which would have been found by a hydrogen thermometer, supposing that the calibration and the interval 100° to zero of the mercury thermometer are exact.

Temperatures,	110°	120°	130°	140°	150°	160°	170°	180°
A . .	—0.05	—0.12	—0.20	—0.29	—0.40	—0.52	—0.65	—0.80
B . .	+0.02	+0.05	+0.09	+0.15	+0.20	+0.26	+0.32	+0.37
C . .	+0.02	+0.04	+0.09	+0.16	+0.25	+0.33	+0.35	+0.34

Temperatures,	190°	200°	210°	220°	230°	240°	250°	260°
A . .	—1.01	—1.25	—1.53	—1.82	—2.16	—2.55	—3.00	—3.44
B . .	+0.35	+0.30	+0.25	+0.20	+0.15	+0.10	—0.05	—0.20
C . .	+0.32	+0.27	+0.18	+0.08	—0.02	—0.14	—0.26	—0.39

Temperatures,	270°	280°	290°	300°	310°	320°	330°
A . .	—3.90	—4.48	—5.10	—5.72	—6.45	—7.25	—8.22
B . .	—0.38	—0.52	—0.80	—1.08	—1.45	—1.80	—2.40
C . .	—0.50	—0.63	—0.88	—1.21	—1.60	—2.03	—2.48

The immediate measures made with the thermometers referred to in the above table were corrected for errors of calibration and for errors in the value of the degree. This latter correction should always be made after determining the number of degrees corresponding with the interval 100° to zero, and the previous remarks upon the errors of calibration show how far it is necessary to take these into account in ordinary thermometric work. It will be seen that the corrections of the column C do not differ greatly from those found by Regnault with ordinary French glass, but are widely different from those of the column A.[1]

In my experiments the curves which represent the corrections for each thermometer show greater departures from the mean curve C as the temperatures increase, but the greatest differences found were only 0.3° at 200°, 0.5° at 300°, and 0.8° at 330°. These figures represent the extreme errors which are probable on using the column C to correct results with thermometers made at Paris. The German thermometer was not among those which showed the greatest divergence, so that the column C may be considered as applicable to soda glass thermometers, but some experiments made with a number of German thermometers induce me to believe that their average corrections should be slightly lower than those of the column C.

Thermometers with a Limited Scale.[2]

Thermometers of this kind have been frequently used within the last few years to meet the difficulty of heating the entire mercury column, and it is generally recognised that it is inexpedient in ordinary experiments to attempt to make a correction for the portion of the scale which cannot be heated. Thermometers with a short scale have a reservoir blown in the glass about 1 cm. above the bulb in order to contain the mercury corresponding to the number of degrees that it is intended to suppress. The total length of the useful part of the scale is about 15 cm., but it is advisable to prolong the stem some 15 cm. more for the convenience of fixing the thermometers in a boiling apparatus.

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[1] It is not probable that these differences are to be attributable entirely to the composition of the glass, and in a paper published in the Comptes Rendus, 6 Nov. 1882, I have pointed out certain features of Regnault's method of operating which lead me to suppose that his corrections are too high.

[2] Thermometers of this kind made at Paris give the zero point and temperatures commencing with about 10°, 20°, 100°, 150°, and so forth. In Germany, thermometers are much used which have the bulb only partially filled and whose scale runs from 98° to 360°.

This mode of construction has some disadvantages which it is most important to remedy, since thermometers of this kind are the only ones which should be applied in accurate work at high temperature.

1. The rise of the zero point is particularly hurtful because the mercury at zero eventually stands in the reservoir and the verification of the zero point becomes impossible. These thermometers should always be subjected to the preliminary treatment which has been described in order to prevent the rise of the zero point.

2. The determination of the fixed points which limit the scale of these thermometers (for example the points 200° and 300°) has hitherto been made by methods far less accurate than those which are used for determining the points zero and 100°. If the constructor has determined these points by comparison with a standard thermometer in an oil bath, errors of 5° are not uncommon, and much larger ones have been noticed. The only expedient which suffices to give results which can be compared with those obtained by observing the boiling point of water and the melting point of ice, consists in using a similar method for high temperatures. I have not succeeded in finding any melting points constant enough for this use, but the boiling points of several pure substances can be employed like that of water. Geissler introduced several years ago the use of naphthalene[1] for this purpose, and this step is a most important improvement; but he does not appear to have determined the boiling point of naphthalene with an air thermometer, and the temperature which he gives is about one degree too low.

After having examined a great number of substances boiling between 150° and 360° I have only found two that unite all the qualifications which fit them for this use; they are naphthalene and benzophenone.[1]

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[1] Dr. Geissler was kind enough to send me some of the naphthalene which he was in the habit of using, and I found it quite pure. The lower boiling point which he has given is not necessarily in error, if the determination was made with a soda glass thermometer, because such an instrument might really give at 218° about 0.5° lower than the air thermometer, and an imperfection in the boiling apparatus used would easily account for the remainder. Geissler's thermometers do actually mark about 1° too low at this temperature.

It is not necessary that these bodies should be absolutely pure, provided the impurities do not affect the boiling point, and some criterion can be established to mark the requisite degree of purification. It was found that the boiling point of commercial naphthalene did not vary more than 0.10° when it had been purified by any method (chemical or physical fractional distillation or crystallisation) until the melting point was brought to 79.9°–79.6°.

The same is true of benzophenone prepared by means of oxychloride of carbon, when it is purified until its melting point is at 48.0° to 47.7°. It will be seen that considerable limits can be tolerated in the melting points without an equal change in the temperature of the boiling point; in other words, the common impurities cause the melting point to vary, while they have nearly the same boiling point. This quality was regarded as indispensable for the use in view, and it was found necessary to reject diphenylmethane and other substances because they do not fulfil this condition. Bodies like essence of turpentine, which are capable of isomeric changes on heating, alcohols which absorb or give off water, ethers which are decomposed by moisture, as well as most acids, chlorides and similar bodies, are unfitted for the purpose.

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[1] A mode of preparation of benzophenone, which was given by Friedel, Crafts and Ador (Comptes Rendus **85**, 672), renders the preparation of this substance possible on a large scale and with the necessary purity. The details of the process will be given elsewhere, but it may be well to indicate one or two points which show that it can be applied without difficulty in a manufactory of chemical products. Oxychloride of carbon is made to act upon benzene in the presence of chloride of aluminium. No difficulty is found in regulating the supply of carbonic oxide when the gas is passed first into a large floating gas-holder containing 50 litres; very simple means suffice to mix in equal volumes chlorine and carbonic oxide, and if the mixture is well made there is scarcely a limit to the rapidity with which it may be passed through a large apparatus in bright sunlight. Three glass balloons of 10 mm. capacity each were used, and the combination takes place chiefly in the first with a considerable evolution of heat. In diffused light the current of the two glasses must be relatively slow.

When carbonic oxide has been used in slight excess the product frequently contains no free chlorine, and in any case an excess of chlorine may be conveniently removed by passing the product into a fourth balloon containing a little benzene exposed to the sunlight. Under the circumstances this absorbent for chlorine is more convenient than zinc or antimony; the rate of formation of oxychloride of carbon can be estimated by condensing it in benzene cooled first with ice and then with a freezing mixture. 100 grams an hour can be obtained with great regularity, and the chloride of aluminium can be subsequently added to this mixture, or the oxychloride of carbon can be passed directly into benzene to which 25 per cent. chloride of aluminium has been added. When the benzene used has been purified by distillation or by fractional crystallisation until its melting point is above 4.5°, the crude benzophenone contained in the reaction is almost pure. It varies only about ½ degree in its boiling point, and the subsequent complete purification is easy.

A primary requisite for this purpose is stability on heating. That of naphthalene is well known, and the inalterability of benzophenone, when boiled for 10 days even under pressure, was tested with perfectly satisfactory results. The vapor density of benzophenone is normal even at a red heat.

The boiling points of pure naphthalene and benzophenone were determined with great care by means of the hydrogen thermometer under pressures varying from 85 mm. to 1800 mm. and a formula found representing their vapor tension. These results, which will be described elsewhere, give the means for heating at will to any fixed temperature between 100° and 360°.

It will be sufficient for our present purpose to give in the following table the boiling points of these two substances under the ordinary atmospheric pressures.

Vapor Tensions.

Naphthalene.		Benzophenone.	
Temperature.	Millimetres.	Temperature.	Millimetres.
215.7	720.39	303.7	723.95
215.8	722.05	303.8	724.77
215.9	723.69	303.9	726.29
216.0	725.34	304.0	727.80
216.1	727.00	304.1	729.33
216.2	728.65	304.2	730.86
216.3	730.31	304.3	732.38
216.4	731.98	304.4	733.92
216.5	733.65	304.5	735.45
216.6	735.32	304.6	736.98
216.7	736.99	304.7	738.52
216.8	738.67	304.8	740.06
216.9	740.35	304.9	741.60
217.0	742.03	305.0	743.14
217.1	743.72	305.1	744.69
217.2	745.41	305.2	746.24
217.3	747.10	305.3	747.79
217.4	748.80	305.4	749.36
217.5	750.50	305.5	750.91
217.6	752.20	305.6	752.47
217.8	753.90	305.7	754.03
217.9	755.31	305.8	755.60
218.0	759.02	305.9	757.17
218.1	760.74	306.0	758.74
218.2	762.46	306.1	760.32
218.3	764.18	306.2	761.90
218.4	765.91	306.3	763.48
218.5	767.63	306.4	765.06

Apparatus for Vapor Tensions.

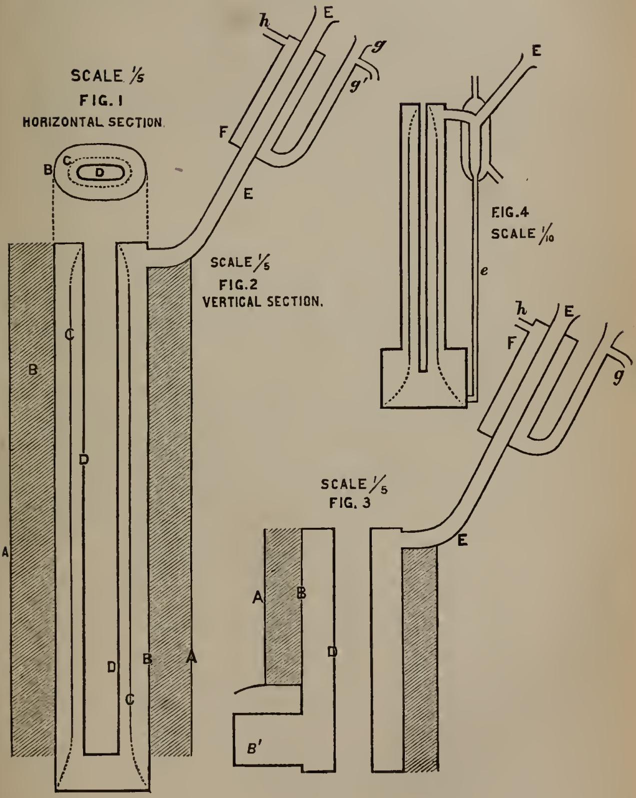
Under the atmospheric pressure the above substances can be used for fixing the scales of thermometers or for correcting them in any kind of glass apparatus, and when a thermometer is to be used for ordinary distillations the corrections can be most conveniently made by boiling in the same vessel some substance of known boiling point falling nearly at the same temperature; and if the scale cannot be entirely heated, the same number of degrees may be left outside in the two cases to be compared. With proper precautions a series of corrections can be thus established with an error of less than 0.5°; but the temperatures that are read off on the thermometers under these circumstances are not usually the true ones, and the corrections must be based upon the known boiling points of the standard substances, which have been determined with special care. Some directions regarding the use of corrected thermometers with a limited scale are given further on under the heading Distillation, but a greater accuracy has been aimed at with the standard apparatus destined for the manufacture or the exact correction of thermometers. The chief difficulty is to avoid superheating the lower strata of vapor, when a column high enough to envelop the scale of the thermometer is heated. If, for instance, benzophenone is boiled in a large glass vessel, with a neck at least 5 cm. wide, it requires a very powerful heat to maintain a column of vapor 30–40 cm. high, and an ordinary long thermometer is found to vary 2 to 3 tenths of a degree according as it is raised or lowered a few centimeters in the vapor.

Considerably better results are obtained by surrounding the neck of the flask with a non-conducting jacket of plaster or mineral wool, and following in the direction thus indicated, various forms of metallic apparatus were constructed, in which a sensitive thermometer with a short scale showed the same temperature to within less than one-tenth degree when placed at any height above the boiling liquid.

Figures 1 and 2 represent a copper apparatus specially adapted to the graduation of thermometers. The metal is 2 mm. thick and will bear a pressure of two atmospheres. All the parts are brazed. The space between the true apparatus *B* and an outer cylinder *A* made of stove-pipe is 3½ cm. It is filled with mineral wool to prevent radiation. *B* is 8 cm. largest diameter and 47½ long. The section Fig. 1 shows its elliptical form, and the smaller diameter is 5½ cm. *C* represents an inner tube of thin copper intended to protect the vapors from condensation. It is pierced with holes as shown by the dotted portions near the bottom and the top. The vapors rise principally between this tube and *D*, and the condensed liquid runs down the sides of *B*. *D* represents a flattened tube 3 cm. by ½ cm. in section and 43 cm. long. It contains 5 or 6 thermometers, which can be conveniently observed together by means of a telescope. When the thermometers are nearly of the same size they may all be held at the requisite height by the slight pressure of a single spring clamp, or they may be grasped by a series of watch-spring clamps or simply suspended from threads. An easy adjustment of the height is important. The vapors are condensed in the tube *E*, and the condenser is of a peculiar form to prevent the stoppage of the tube by the solidification of crystalline substances. Water is allowed to flow constantly into *g*, and out drop by drop at *g′*, and the water consequently remains always at the level of *g′* in the condenser. The water is soon heated to boiling, the steam escapes at *h*, and the vapors of naphthalene and other substances are condensed at 100° instead of at the ordinary temperature, and flow back as liquids. In an ordinary operation it is not even necessary to renew the water, and it is only when the heating is long-continued that a flow of water becomes necessary. For substances which like benzoic acid melt higher than 100°, the water may be replaced by amylic alcohol or by some other convenient liquid, and a lead tube (not shown in the figure) soldered upon *h* can be so arranged as to return the amylic vapors in the form of liquid to the condenser at *g*.

The apparatus of Figs. 1 and 2 is long enough to heat any ordinary thermometer, but when a great subdivision of the scale makes it of unusual length, the protruding portion of the stem is heated to the same temperature by the cylinder (Fig. 3), which is put upon the top of the first, and contains the same standard substance. The non-conducting jacket is so arranged as to allow the flame to play around *B*, and this part of the cylinder projects enough to allow a lamp to be placed under it. Any number of such cylinders may be superposed, so that there is no limit to the length of a thermometer which may be heated to a fixed temperature without danger of superheating the vapors.

Several questions regarding the accuracy of this method of fixing temperatures required to be studied experimentally.



SCALE 1/5
FIG. 1
HORIZONTAL SECTION.

SCALE 1/5
FIG. 2
VERTICAL SECTION.

FIG. 4
SCALE 1/10

SCALE 1/5
FIG. 3

The temperature was found to be exactly the same whether the interior tube *D* was used as an air-bath or was filled with high-boiling paraffin, and the use of oil or paraffin was rejected because it has many inconveniences. The tube *D* can be made cylindrical and of much larger dimensions to fit it for air thermometer work, without making any difference in the temperature, when the mouth is well stopped with asbestos.

It was thought possible that the condensed liquid from *E* flowing back along the sides of *D* might lower the temperature, and comparative experiments were made with the apparatus described and with that represented on a smaller scale (Fig. 4), in which the vapors are so condensed as to be returned by the small tube *E* to the bottom of the apparatus. The results were identical in each case.

Other experiments were made by enlarging the bottom of the cylinder and by varying the quantity of the liquid, and it was found that such variations made no difference in the temperature, provided radiation of heat was well guarded against. The simplest form, Figs. 1 and 2, was therefore chosen, and it is believed that it is well adapted to obtaining the true boiling point of a high-boiling substance, as Rudberg's (Regnault's) apparatus is to measuring the boiling point of water.

A smaller apparatus, in which the interior tube *D* is cylindrical and only 5 mm. in diameter, is used for examining a single thermometer, and it can be used more quickly since it requires only 6 to 8 minutes for the temperature to become stationary. With the larger apparatus a longer time is required, and the error which is most likely to occur on working with it arises from not waiting patiently until the mercury column has become stationary.

The thermometers are plunged in the tube *D* so that at the moment of reading only about 1° appears above the top. This requires a certain adjustment, which can be made after they have been heated about ten minutes ; and since this operation may bring cool parts of the stem in contact with the tube *D*, and change the temperature of the air-bath, 8–10 minutes must usually elapse after the final adjustment before the temperature becomes constant and before the final reading should take place. For this cause there is even a certain advantage in replacing the single tube *D* by a number of smaller ones, each containing a single thermometer.

The liquid must be made to boil constantly, so that the condenser is heated with about equal rapidity in all determinations, a point which there is no difficulty in appreciating.

All these forms of apparatus can easily be connected at *E* with a reservoir of about 20 litres capacity, filled with air at any pressure, and no difficulty was found in boiling naphthalene and benzophenone under pressures varying from 100 to 1500 mm., so that any temperature within the ordinary thermometric scale can be determined, and the apparatus can thus be used for correcting or for graduating the whole scale.

The examination of different points in the scale of a thermometer by means of such an apparatus may replace advantageously all the corrections arising from errors of graduation, calibration, and the departure from the air thermometer scale. The operation is more accurate and infinitely less tedious than the usual ones for temperatures higher than 100°.

Corrections for Thermometers with a Limited Scale.

If the points 100° and 218° or 218° and 306° are so fixed on the scale of the mercury thermometer that they exactly agree with the measures that would be obtained by a hydrogen thermometer, a different table of corrections must be used to bring determinations made on intermediate points of the scale in agreement with the hydrogen thermometer, and the following tables give these corrections for each case of a limited scale. The 1st horizontal column gives the temperatures, and the 2d the corrections that are to be applied (taking notice of the signs + or —) to transform degrees on the mercury thermometer into two measures of temperature as determined by the hydrogen thermometer.

Table No. 1—*Scale* 100°–218°.

Temp. .	100°	110°	120°	130°	140°	150°	160°	170°
Correc. .	0.00	+0.01	+0.02	+0.07	+0.13	+0.21	+0.28	+0.29

Temp. .	180°	190°	200°	210°	218°	220°	230°
Correc. .	+0.28	+0.25	+0.19	+0.09	+0.00	—0.02	—0.12

Table No. 2—*Scale* 218°–306°.

Temp. .	210°	218°	220°	230°	240°	250°	260°
Correc. .	—0.06	0.00	+0.02	+0.09	+0.15	+0.21	+0.26

Temp. .	270°	280°	290°	300°	306°	310°	320°
Correc. .	+0.33	+0.37	+0.30	+0.15	0.00	—0.06	—0.31

As it is supposed that the thermometers intended for this use have been subjected to a preliminary treatment at 355°, no great permanent displacement of the zero point can take place in subsequent experiments, and with a limited scale the extent of the temporary depressions and elevations of the zero point is not large; however, in accurate work this point should always be observed after a measure of temperature, and a correction made for its displacement, and the above tables are adapted to results thus corrected.

In these thermometers the value of the degree is derived from a verification of the terminal points of the scale by means of boiling water, naphthalene or benzophenone, and if these points are inexact on the mercury thermometer, all the measures must be multiplied by the fractions representing the true value of the degree. The terminal points on the scales of these thermometers are to be determined for graduation or for verification by observing first the higher temperature, and it is well to heat several hours at this temperature to avoid any considerable displacement of the zero during graduation. The lower point is then determined as rapidly as possible.

It may be noticed that the corrections are very small compared with those which are applied to the ordinary scale running from zero to 360°, and they are almost identical for all thermometers. If smaller limits are taken for the scale, and points are fixed 50° apart in accordance with a gas thermometer, the corrections are so small for the intermediate points that no series of determinations which have been thus far made with the air thermometer are accurate enough to determine them with certainty; and the agreement between the scales of different instruments, which becomes closer as the points are taken nearer together, may be considered as almost perfect when the intervals are only 50°, and sufficiently exact for all common uses when the intervals are about 100°.

The Evaporation of the Mercury in the Thermometer.[1]

When the thermometer has been made entirely vacuous of air, a rapid evaporation of mercury may be observed even at 100°, when the whole of the stem is heated in steam. If the necessary precautions are taken to set aside all other influences which would change the height of the mercury column, it may be observed to fall from minute to minute when it is watched with a good micrometric telescope; and after a quarter of an hour a variation of 0.01° or 0.02° is noticed. At high temperatures the evaporation of mercury is much more rapid, and is frequently a source of great inconvenience, disturbing the observations and dividing the mercury column by the condensation in the cooler parts of the stem. The evaporation is quite appreciable in experiments which last several days, even when the mercury is only heated 10° or 20° higher than the temperature of the air. When air is left in the stem of the thermometer the evaporation of the mercury is much retarded; but even in this case, when the stem of the thermometer is heated to 250°, a loss of mercury equivalent to several tenths of a degree may take place within half an hour. If the zero point is observed after each measure of temperature as has been recommended, the apparent sinking of temperature caused by the evaporation of the mercury does not give rise to an error.

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[1] This phenomenon has been noticed by every one who has paid attention to thermometric measures, and has even been mentioned in some publications; but the errors which it may entail seem sometimes to have been neglected, and it will be seen by what has been said above that the evaporation of mercury might be a permanent cause of error in the results obtained with thermometers whose stem is left open to the air when they are heated to high temperatures.

The Purity of the Mercury in a Thermometer.

If the mercury which is used to fill a thermometer has not been well purified, or if it has not been boiled long enough in the thermometer to free the bulb and stem from air adhering to their sides, the mercury column is divided by air bubbles after long use at high temperatures. Even if the air bubble is driven into the upper reservoir, another one frequently forms in the same place, and such a thermometer becomes entirely useless. Even when it is intended to leave air in the upper reservoir, the boiling ought to be carried out as in a thermometer which is to be left vacuous, and it is advantageous to boil the mercury while the thermometer is connected with a Sprengel's pump. It seems probable, from the observations that have been made with thermometers and barometers, that when a layer of air or moisture has been left between the mercury and the glass it may serve as a channel by which further quantities of air or moisture may penetrate, and inconveniences are noticed with such instruments which certainly do not occur with those which are made with great care.

According as thermometers are well or ill made in these respects every degree of excellence may be noticed between those which will not bear a single heating, even of a few minutes at 200°, without having the column broken, and those thermometers which are so well made that they may be heated for many days at 355° without showing the slightest air bubble in the bulb. This last was the case with four out of eight thermometers heated for eleven days and nights at 355°.

The preliminary treatment of thermometers at high temperatures, which has been frequently referred to, brings out these defects in the manufacture, and those instruments which will not bear the test must be rejected.

In connection with this subject may be mentioned a paper by Mr. Wiebe.[1] This author has repeated and confirmed my experiments upon the diminution of the coefficient of expansion of glass which accompanies a permanent contraction of the bulb of a thermometer, and he has published a series of interesting observations on the relation between the two phenomena which are in accordance with the principal results of my experiments. On the other hand, he considers that the permanent elevation of the zero point (in other words, the contraction of the bulb) cannot be considered as principally due to the causes which I have assigned. This opinion is partly founded upon Mr. Wiebe's incorrect determinations of zero point depressions. Those published by him for the temperature 370° are probably less than one-third of the true value; and he appears also to have been misled by a theory which it will be interesting to examine. Mr. Wiebe supposes that a gas is disengaged from the glass on heating, and that a portion of the contraction of the bulb is due to this cause. He cites the experiments of Dumas, Lockyer, Miller, who have found that several metals, as well as phosphorus, give off a gas when they are strongly heated *in vacuo*.

It might be objected that these experiments would be little conclusive if it were true that glass and porcelain were like the metals in this respect, because these substances formed the material of the apparatus which was used. But let us suppose that a contraction may really result from the disengagement of a gas which fills the intermolecular spaces of glass; we may calculate the probable extent of the contraction by taking the necessary data from well-known experiments with palladium. This is the only metal with which the phenomenon has been studied with reference to the contraction of a solid body produced by a loss of gaseous material. It may be added, however, that the results would be six or eight times more favorable to the hypothesis of Mr. Wiebe if they were based upon the solution of hydrochloric acid or of ammonia in water.

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[1] Metronomische Beiträge, No. 3.

Mr. Wiebe has given no measures of the quantity of gas which was observed on heating and which separated the mercury column in his thermometers. The volume of the gas can be measured when the mercury is not made to boil, and I will take the largest quantity which I have observed as a basis for a calculation. During an elevation of the zero point equal to 17°, a bubble of gas was formed on the side of the bulb; this was eventually brought into the stem, where it separated the column of mercury and filled a space equivalent to 1.35°. The contraction of the bulb was equivalent to 0.0026 part of the total volume occupied by the mercury. This latter volume may be taken as unity, and the quantity of gas disengaged was equivalent to 0.00021 part. The volume of the glass of the bulb relatively to the mercury may be taken at 0.2, which is a usual proportion in thermometers whose bulbs and mercury are weighed for specific heat determination. (The relative volume of the glass in my thermometer was really larger.) We will suppose that only half the gas is emitted into the interior of the thermometer. We will suppose that the contraction of palladium is proportional to the quantity of hydrogen disengaged. (It is really smaller when the volume of hydrogen is small.)

It would result that a diminution of volume from 1.0026 to 1.0000 would be accompanied by an evolution of more than 15 volumes of gas. Divide this number by 2 to express that only the half of the gas disengaged by the glass of the bulb appeared in the interior of the thermometer, and by 5 because the volume of the glass is supposed to be only equal to one-fifth that of the mercury, and we find that 1.5 volume of gas should be given off if the contraction were due only to this cause.

It may be concluded that the quantity of gas disengaged in the experiment most favorable to the theory of Mr. Wiebe was 7000 times smaller than the quantity required by the calculations founded on the above hypotheses, or that $\frac{1}{7000}$ of the effect is attributable to a disengagement of gas. This discrepancy becomes still greater when it is remembered that the bubble measured was not under atmospheric pressure, as assumed in the calculation, but under a much smaller pressure, and in the experiments where no gas was disengaged no part of the phenomenon is accounted for by Mr. Wiebe's hypothesis.

It may also be observed that, did the glass of a thermometer evolve a gas in sufficient quantity to account for a notable contraction of the bulb, the pressure of this gas would be quite appreciable, even in thermometers which have an upper reservoir, while in those which have none and are particularly intended for use at high temperatures, the pressure might amount to several hundred atmospheres at a moment when the stem is filled with mercury, leaving a free space of only some 50°.

I have taken the only data known regarding a solid; but, as has already been remarked, the numbers would be more favorable to the views of Mr. Wiebe if the calculation were based upon the absorption of hydrochloric acid or ammonia by water, and the discrepancy between the facts and the theory would be reduced from 7000 to 700 if the gas were supposed to be oxygen with the same density, when condensed to a liquid, as water.[1] But these numbers, ranging in my experiments from 700 to infinity, indicate too strong probabilities against the hypothesis in question to make it worth further consideration.

This subject has been treated under the heading of "Purity of the mercury in a thermometer," because it is believed that the vexatious appearance of bubbles is usually due to want of care in the manufacture of thermometers. It may be added that at temperatures so high as 370°, particularly when the mercury boils, a rapid movement of the column may imprison air from the reservoir, and that wherever a bubble has once formed it is apt to reappear. Perhaps, as has been said, the *moistening* of the glass by a gas may extend to the formation of a permanent canal along the stem, between the mercury and the glass, through which gas passes, particularly when the mercury is in rapid movement. The following experiment has some bearing on the subject: A clean capillary tube, plunged deep under the surface of mercury, serves to suck up an unbroken column of mercury; but even a short exposure of the tube to the air of a laboratory coats it with a film of chloride of ammonium, and then when the mercury is made to flow up through it, bubbles of air are drawn down between the mercury and the outside of the capillary tube, and a broken column appears in the tube. Thus, a thermometer which has not been sufficiently cleaned is particularly liable to the defect of the formation of bubbles.

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[1] The theory of M. Dumas and the experiments of M. Raoul Pictet indicate the density of liquified oxygen is about 1.

The Influence of Pressure upon a Thermometer.

The most complete series of experiments upon this subject has been made by Mr. Mills, who has studied the relation between the rise of the mercury in the stem and the pressure exercised upon the bulb of the thermometer. In one series of his experiments the rise was 0.106° for every atmosphere of pressure up to 133 atmospheres.

According to Mr. Mills, an excess of pressure of 1 atmosphere causes a rise of about 0.2°; but this factor must be determined for every thermometer separately. It appears to be in inverse ratio with the thickness of the glass, but depends also upon the form of the bulb; and it is evident that a fault in the symmetry of the bulb might considerably increase the compressibility of a thermometer.

It is apparent from the above figures that the variations in the barometric pressure may be neglected from this point of view; but it is frequently necessary to take into account the differences of pressure, which depend upon whether the thermometer is placed horizontally or vertically, and, in a long thermometer, the variations of the zero, or better, of the boiling point, which ensue upon a change of position, may be used to calculate approximately the coefficient of compressibility of a thermometer.

Variations of this kind must be allowed for in distillations *in vacuo*, and in all similar operations where the thermometer is subjected to a diminished or increased pressure; but it is frequently preferable to avoid such corrections by placing the thermometer in a very thin tube, closed at its lower extremity, and communicating with the air at its upper end. For another reason it is frequently convenient to enclose the thermometer in an extremely thin glass tube, like those which are used for making the stems of areometers, in order to prevent the black coloring matter (usually a mixture of wax and lampblack) from being dissolved away from the division marks on the scale. If the tube is thin and of nearly the same diameter as the thermometer, and a little mercury is put in the bottom to cover the bulb, the sensitiveness of the thermometer is very little diminished, and thermometers so arranged respond more quickly to change of temperature than those of the German model, which have a portion of the bulb covered by a great thickness of glass at the point where an exterior tube containing the scale is soldered to the bulb.

Distillation.

When the substance is pure, and when the above precautions regarding the use of thermometers have been observed, errors in the determination of the boiling point arise most frequently from too hasty operations. The mercury in the bulb takes the temperature of the vapors almost immediately, but the same is not true of the mercury column in the stem, which has to be heated through a great thickness of glass, and, what is of still more consequence during this process, the liquid which is at first condensed very rapidly on the upper part of the stem runs down and cools the bulb. Even when all the mercury column is surrounded by the vapor of the boiling substance, and the apparatus is in every way well arranged to guard against loss of heat, 5 to 10 minutes are required for the temperature to become constant, and during this period the apparatus should be held in such a position that the liquid in the condensing tube may flow back, and from time to time during the distillation it is well to heat for a few moments without allowing any substance to pass over into the recipient in order to see if a constant temperature has been attained.

With substances boiling at a very high temperature it is somewhat difficult to obtain a column of vapors sufficiently long to heat the stem of the thermometer without overheating the vapors near the bulb. And where the metallic apparatus before described cannot be used, the difficulty of dealing with high-boiling substances is greatly lessened by surrounding the apparatus with a jacket at least 2 cm. in thickness of plaster of Paris or asbestos cloth, leaving only a portion of the bottom of the boiling vessel exposed to the flame. This portion can be usually entirely covered with the substance which is to be distilled, so that the flame does not at any point come in contact with the part of the apparatus containing the vapors. When plaster of Paris is used, such an apparatus must be maintained 2 or 3 hours at high temperatures before the water is evaporated out of the plaster, and in fact the moment when the apparatus is ready for use can be observed by the very much smaller flame required to maintain active ebullition. When the glass apparatus has a disengagement tube soldered into its neck the plaster must not be allowed to set at the joint, it should be scraped away from the part while soft, although the protecting jacket should be carried about 2 cm. higher round the neck. Where a substance is known to have the same boiling point at the beginning and at the end of a distillation, or when the quantity of the substance is too small to admit of a fractional distillation, the boiling point may be conveniently tested in an ordinary test tube surrounded by a plaster cylinder; for instance, if sulphur is made to boil in this way, the plaster becomes dry after 2 or 3 hours, and then the condensation takes place almost entirely on the part of the naked tube immediately above the plaster cylinder. A cylinder so prepared and dried may be slipped over other test tubes and used for all boiling point determinations. Experiments with such an apparatus filled with mercury or sulphur, and using an air thermometer, have shown that the boiling point determinations are reliable to within 0.2°.

Melting-point Determinations.

When a sufficient quantity of substance can be disposed of, it is best to introduce a small and sensitive thermometer into the liquid, and to observe all the changes of temperature during the complete solidification.

It is usual to take melting points of small quantity of matter in a capillary tube attached to a thermometer, and both are heated in a sulphuric acid bath or in a paraffin bath[1] for temperatures higher than 300°. It is only necessary to remark upon a modification of this process in which the apparatus contains an interior tube, which is used as an air bath, surrounded by sulphuric acid. This form of apparatus was devised to prevent the sulphuric acid vapors from escaping into the air, and to prevent the acid from attracting moisture. These ends could be obtained more simply otherwise, and the apparatus has a grave defect. It is only necessary to heat a large and a small thermometer together in an air bath at changing temperatures to see that one is constantly behind the other in its indications, and it is quite certain that a small mass of substance in a capillary tube would be usually heated more quickly than a thermometer placed beside it, when they are both heated in an air bath at rising temperatures. It is therefore indispensable in melting point determinations to heat the thermometer and the capillary tube together in a liquid, and not in any form of air bath. The numerous forms of apparatus proposed for observing points of fusion have often been applied with good results to special cases, but the ordinary method is on the whole the most convenient, and few substances are known of sufficient purity to demand a process of greater accuracy. The method which is most nearly perfect is that which is always used with melting ice, and it would be interesting to heat such other solids as can be obtained pure in sufficient quantities in an air bath at a temperature somewhat higher than their melting points and to observe the degree of constancy attained by a thermometer properly surrounded by the melting solid.

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[1] It is not difficult to find English paraffin candles, which are so well purified that after distilling a small portion of the more volatile hydrocarbons it enters into active boiling above 370°.

ON THE ACTION OF ALDEHYDES ON PHENOLS.

I.

By Arthur Michael.

The investigation of the action of aldehydes on phenols was begun by A. Baeyer,[1] shortly after the discovery of the phthaleïns. It was found that by heating benzoic aldehyde with pyrogallol a resinous compound of the composition $C_{26}H_{22}O_7$ was formed. Concentrated sulphuric acid on a mixture of benzoic aldehyde and resorcin gave a reddish resin, and amorphous compounds are formed in the action of sulphuric acid on mixtures of ethylaldehyde or chloral and phenol or pyrogallol. In the following paper[2] Baeyer used a large quantity of concentrated chlorhydric acid to obtain the resin $C_{26}H_{22}O_7$ from benzoic aldehyde and pyrogallol. When the mixture was heated, besides the reddish resin, a crystalline compound was obtained. This compound, which is isomeric with the resin, was more easily obtained by adding the acid gradually to a boiling alcoholic solution of benzoic aldehyde and pyrogallol. Salicylaldehyde and pyrogallol gave, under similar conditions, the compound $C_{26}H_{22}O_9$; while from benzoic aldehyde and naphthol the compound $C_{34}H_{26}O_3$ was obtained. These compounds are formed from an equal number of molecules of aldehyde and phenol by the loss of an equal number of molecules of water; $2C_6H_5—CHO + 2C_6H_3(OH)_3 = C_{26}H_{22}O_7 + 2H_2O$. In a third communication[1] it was stated that concentrated chlorhydric acid acting on mixtures of methylal and phenol or resorcin gave resins, while pyrogallol and gallic acid yielded a small amount of crystalline products. None of these products have been since examined, but a number of investigations on the action of aldehydes on phenols, under somewhat different conditions, came from Baeyer's laboratory in the following years. Jaeger[2] obtained, by the action of a large quantity of concentrated sulphuric acid on a mixture of chloral and thymol, the compound $CCl_3—CH(C_{10}H_{12}OH)_2$. Ter Meer,[3] in a similar manner from methylal and methylphenyloxide, the compound $CH_2 = (C_6H_4OCH_3)_2$; and from chloral and phenol, $CCl_3—CH = (C_6H_4OH)_2$ was obtained. Later, by using tin tetrachloride instead of sulphuric acid, a condensation product of ethylaldehyde and phenol was obtained. Fabinyi[4] from ethylparaldehyde and phenol obtained a small yield of ethylidenediphenol, $CH_3—CH(C_6H_4OH)_2$; and Steiner,[5] from chloral and thymol, trichlorethylidenedithymol. Very recently, C. Etti,[6] in the Vienna University laboratory, by the action of a large quantity of concentrated chlorhydric acid (50 parts to one part of aldehyde), believes he has obtained from vanillin and pyrogallol the crystalline compound $C_{20}H_{18}O_8$; from vanillin and phloroglucin an isomeride of that compound. I shall return to Etti's investigation towards the end of this paper. The one result common to all these investigations is the formation of complicated substances from aldehydes and phenols by linking of carbon to carbon, and elimination of water. Beyond this there is considerable discrepancy. Baeyer obtained by the action of equal molecules of benzoic or salicylic aldehyde and pyrogallol, compounds formed by the elimination of an equal number of molecules of water; while Etti obtained from a different aromatic aldehyde, vanillin, and pyrogallol, under the same conditions, a compound derived from one molecule of aldehyde and two molecules of the phenol with a loss of one molecule of water. The last reaction is the type of that occurring between methyl or ethylaldehyde and phenols, when sulphuric acid, or tin tetrachloride, is used as the dehydrating agent. Are these differences due to inherent properties of the aldehydes, or to the somewhat different conditions of the experiments? In all these experiments it is supposed that the presence of a strong dehydrating agent is a necessary condition. What relation exists between the resin obtained from benzoic aldehyde and pyrogallol, and the crystalline compound obtained under slightly different conditions? In regard to the constitution of the compounds that have been obtained from aromatic aldehydes and phenols, absolutely nothing is known. Has this resin-formation from aldehydes and phenols a connection with the formation of resins in the vegetable world? In other words, have the contents of the cells the property of forming these resins? and do they resemble in their properties those found in nature? These are some of the questions that led to a reinvestigation of the action of aldehydes on phenols.

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[1] Berichte der deutschen chemischen Gesellschaft, **5**, 25.

[2] *Ibid.* **5**, 280.

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[1] Berichte der deutschen chemischen Gesellschaft, **5**, 1094.

[2] *Ibid.* **7**, 1197.

[3] *Ibid.* **7**, 1200.

[4] *Ibid.* **11**, 283.

[5] *Ibid.* **11**, 287.

[6] Monatshefte für Chemie, **3**, 637.

In the present paper I shall confine myself to the description of the experiments that have been made in the study of the action of benzoic aldehyde on resorcin. The investigation is coupled with such experimental difficulties that, although considerable time has been spent on it, hardly more than a foothold for future service has been gained. The action of heat on a mixture of benzoic aldehyde and resorcin was first examined. In open vessels the mixture—resorcin dissolves in the aldehyde on heating—may be heated for days without a reaction ensuing. In closed tubes and heated to 200° a resin was formed, which was not examined.

In striking contrast is the readiness with which benzoic aldehyde and resorcin react in presence of acids. Baeyer had already found that concentrated sulphuric acid poured on a mixture of these substances converted them into a red resin. A few experiments sufficed to show that it is advantageous to moderate the violent action by dissolving the aldehyde and phenol in alcohol, and that the function the acid plays in the reaction has been completely misunderstood. If to a solution of one gram of benzoic aldehyde and one gram of resorcin in three grams of absolute alcohol, a drop of concentrated chlorhydric, or sulphuric acid, is added, it will be noticed that as soon as the acid comes in contact with the solution a resinous substance is formed, which immediately dissolves in the alcoholic solution. A rise of temperature takes place, under the above conditions, to 55–60° C., and the solution soon becomes quite thick; at the same time a deposit of a crystalline substance takes place. If the filtered alcoholic solution, after it has cooled, is poured into a large quantity of water, a white amorphous compound settles, which is the first product of the action of the acids on benzoic aldehyde and resorcin. It is easy to prove that the formation of this product is entirely independent of the affinity of the acid for water. A trace of chlorhydric acid, less than $\frac{1}{5}$ of a drop, causes the formation of the same resin, the only difference being that the reaction proceeds somewhat more slowly, and a natural consequence thereof that the solution becomes less warm. Instead of three parts of absolute alcohol, twenty parts may be taken, without changing in the least the final result; or a drop of chlorhydric acid may be dissolved in a considerable amount of alcohol, and then added, with the same result. Nor is absolute alcohol necessary, dilute alcohol will serve the same purpose; only, if too dilute, the resin will separate from the solution as it is formed. Still more conclusive were the experiments proving the resin-formation in the presence of water. If to equal parts of the aldehyde and resorcin and twenty parts of water a drop of chlorhydric acid is added, and the mixture heated to boiling, the aldehyde gradually unites with the resorcin, and is completely converted into the resin. A drop of chlorhydric acid is sufficient to induce the reaction between a considerable quantity of aldehyde and resorcin. In one experiment twenty grams of these substances were completely converted into the resin by a single drop of acid.

To obtain the resin suitable for analysis, a drop of chlorhydric acid was added to a solution of equal parts of aldehyde and resorcin in three parts of alcohol, the solution allowed to cool, filtered, and the filtrate poured into water. The precipitated white resin was extracted several times with a large quantity of cold water, dissolved again in a small amount of alcohol, and reprecipitated by pouring into water. All attempts to obtain this compound in a crystalline form were without success. The white substance, when it contained considerable water, remained unchanged on contact with the air; but it could not be obtained free of water, as it became dark on standing in the air three or four hours. An attempt to dry it in a partial vacuum was also without result. In order to free the substance of water, it is necessary to heat it in an atmosphere of carbon dioxide or hydrogen. The pulverised resin, after being well pressed between filter paper, in a platinum boat, was brought into a tube, one end of which is connected with a series of drying tubes, and these with a Kipp's carbon dioxide generator, and the other end with a calcium chloride tube. The tube is enclosed in a glass jacket, through which steam can be passed. Even after passing a slow current of dried carbon dioxide for forty hours over the resin in the cold, it was found that a decided loss in weight occurred in the next four hours. Moreover, notwithstanding the precautions taken to prevent the ingress of air into the apparatus, the substance had taken a decided reddish tinge. Heated to 100° in a current of carbon dioxide, the resin melted, a property which is due to the presence of water, and gave off, comparatively, a very considerable amount of water. It is probable that it either contained water in the form of so-called water of crystallisation, or the action of heat caused a condensation. The reddish resin, which when dry did not melt at 100°, and powdered had but a slight reddish color, gave the following numbers on analysis:

0.1928 gram of substance gave 0.5577 gram of CO_2 and .0977 gram of water.

0.2285 gram of substance gave 0.6601 gram of CO_2 and 0.1135 gram of water.

Theory for $C_{26}H_{20}O_4$.		Found.	
C	78.69	78.83	78.78
H	5.05	5.62	5.51

The white resin, before drying at 100°, is insoluble in boiling water, but melts under it to a reddish mass. It is very soluble in alcohol, benzene, ether and glacial acetic acid. On exposure to the air it gradually takes up oxygen, and is converted into a dark brown substance; a decomposition which takes place very rapidly when the resin is heated. It dissolves very readily in alkalies, to form colorless solutions, which are extremely sensitive to the action of oxygen. The solutions, exposed to the air for several minutes, take a dark brown color.

The properties of the dried resin in reference to solubility and behavior towards alkalies do not differ from the above. It melts, however, only at a high temperature—above 330°—under complete decomposition, and remains solid under boiling water. These differences are sufficient to show that the resin has undergone a decomposition more than the loss of uncombined water. The analysis and properties of the resin, when dried until constant weight in a partial vacuum, show this more conclusively. The red, dried substance gave off water on heating at 100°. No further importance is to be attached to the following analysis than as showing that the substance dried in a vacuum contained water other than mechanically mixed, since the red color of the substance indicated a partial oxidation.

0.2160 gram of substance gave .5491 gram of CO_2 and .1043 gram of H_2O.

Theory for $C_{26}H_{20}O_4$, $3H_2O$.		Found.
C	69.34	69.33
H	5.77	5.32[1]

To obtain the acetyl derivative, the white resin was well pressed out between filter paper, dissolved in five times its weight of acetic anhydride, and an equal weight of fused sodium acetate added. The mixture was heated to boiling for an hour, and then poured in a large amount of water. The precipitate was dissolved in alcohol, filtered, and reprecipitated by addition of water. An analysis gave the following numbers:

0.2150 gram of substance, dried at 100°, gave .5681 gram of CO_2 and .1062 gram of H_2O.

Theory for $C_{26}H_{16}O_4(OCCH_3)_4$.		Found.
C	72.31	72.16
H	5.17	5.48

The white, amorphous acetyl derivative is somewhat less soluble in alcohol and benzene than the mother-substance. It is insoluble in alkalies in the cold. When heated with them it gradually dissolves, the solution becoming dark brown.

The crystals that separate from the alcoholic solution of benzoic aldehyde and resorcin on addition of chlorhydric acid, are formed by action of the acid on the white resin, the first product of the reaction. This may be easily proven by adding a drop of the acid to a clear solution of the resin in alcohol. The temperature of the solution does not change, but soon the formation of a crystalline deposit will be noticed. The amount of the crystalline compound formed is dependent on the quantity of acid added; not, however, on the concentration of the acid. If to the filtrate of the aldehyde-resorcin mixture, after the formation of precipitate caused by the addition of a drop of acid, a second drop is added, a further precipitate is deposited; the amount formed being the same whether the acid is concentrated or previously diluted with alcohol.

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[1] The hydrogen estimation shows that the substance was partially oxidised. The constitution of the white resin is probably $C_{26}H_{20}O_4$, $2H_2O$, or $C_{13}H_{12}O_3$. I shall endeavor to obtain it in form suitable for analysis.

The crystals consist of two substances, one crystallising in needles, and the other in square plates. A convenient method of preparing these substances is based on the action of acids on a solution of the resin in an aqueous solution of resorcin. A mixture of five parts of benzoic aldehyde, ten parts of resorcin, and twenty parts of water, on heating, formed a clear solution. To the hot solution three or four cc. of water containing several drops of concentrated chlorhydric acid were added, and the solution heated on a hot water-bath as long as a precipitate was deposited. The slight reddish precipitate was separated by filtration, and the filtrate, again treated with acid and heated, yielded a further quantity of the crystalline products, which had a decided yellow color. That the first product formed in this method of preparation is the resin was shown by extracting the solution, after heating it for a moment, with ether. The extract contained resorcin and the white resin. The crystalline deposits were extracted several times with a large amount of boiling alcohol, filtered while hot, and the filtrate, allowed to stand, deposited square plates. For analysis they were recrystallised several times from alcohol. The analyses of the substance, dried at 100° in a current of carbon dioxide, gave the following numbers:

0.2038 gram of substance gave 0.5852 gram of CO_2 and 0.0957 gram of H_2O.

0.2082 gram of substance gave 0.5968 gram of CO_2 and 0.1008 gram of H_2O.

	Theory for $C_{26}H_{20}O_4$.	Found.	
C	78.69	78.32	78.13
H	5.05	5.27	5.38

The substance does not decompose on exposure to the air.

0.4769 gram of air-dried substance lost 0.070 gram of H_2O when dried in CO_2 at 100°.

0.2450 gram of air-dried substance lost 0.0357 gram of H_2O when dried in CO_2 at 100°.

	Theory for $C_{26}H_{20}O_4$, $4H_2O$.	Found.	
H_2O	15.37	14.68	14.57

The hydrated compound separates from alcohol in colorless quadratic plates or prisms. It is moderately soluble in hot, very sparingly in cold alcohol; insoluble in water and ether. Alkalies dissolve it readily in the cold, and the solution soon becomes dark on exposure to the air. The addition of acids to a freshly prepared alkaline solution precipitates the substance in an amorphous form. This precipitate retains its amorphous character on boiling with water or acids, but separates from a hot alcoholic solution on cooling in quadratic plates. It melts at a high temperature (above 330°) under decomposition. In a partial vacuum most of the water of crystallisation was given off (C—77.11, H—5.45), but the substance took a decided reddish color. Fused with caustic potash and a small quantity of water, at a low heat, until the addition of acid to a test did not cause a precipitate, the flux dissolved in water. Acidified, and then rendered slightly alkaline with sodium carbonate, it gave resorcin on extraction with ether. In the alkaline solution the presence of benzoic acid was proven.

Acetic anhydride does not dissolve the hydrated substance, even on boiling. A mixture of the substance, anhydride and fused sodium acetate, in proportion of equal parts of substance and salt and five parts of anhydride, gave on heating a clear solution, from which, on heating for several minutes, the acetyl compound completely separated. The crystals were separated by filtration, washed with alcohol and crystallised from boiling xylene. An analysis gave the following numbers:

0.2497 gram of substance, dried at 100°, gave 0.6621 gram of CO_2 and 0.1163 gram of H_2O.

	Theory for $C_{26}H_{16}O_4(C_2H_3O)_4$.	Found.
C	72.34	72.31
H	4.93	5.17

It is moderately soluble in boiling xylene, and separates on cooling in obliquely truncated, translucent prisms, which do not contain water of crystallisation. Insoluble in cold, but sparingly in hot alcohol. Cold alkalies do not dissolve it; when heated a gradual solution is effected, and the solution becomes dark colored. By heating anhydrous $C_{26}H_{20}O_4$ with acetic anhydride and sodium acetate an acetyl compound with the same physical properties was obtained.

To obtain a reduction product the crystalline compound $C_{26}H_{20}O_4$ was dissolved in hot alcohol, and zinc or tin and an alcoholic solution of chlorhydric acid added. From the hot solution white needles gradually separated. These were a compound of zinc or tin chloride with the reduced compound. On decomposition the double compound gave a colored reduction product. In order to reduce in an alkaline solution it is necessary to exclude carefully the presence of oxygen. The alkaline solution in a small flask, through which a slow current of hydrogen gas passed, was treated with sodium amalgam, the liquid poured into dilute chlorhydric acid, avoiding, as much as possible, contact with the air. From the alcoholic solution of the amorphous precipitate crystals separated, which, dried at 100° in CO_2, on analysis gave the following result:

0.2357 gram of substance gave .6822 gram of CO_2 and .1188 gram of H_2O.

	Theory for $C_{26}H_{22}O_4$.	Found.
C	78.38	78.47
H	5.53	5.61

The substance is deposited from hot alcohol on cooling as quadratic prisms with end-faces. It appears to be somewhat more soluble in hot alcohol than the original substance, and also to oxidise more easily. The differences between the percentages of carbon and hydrogen of $C_{26}H_{22}O_4$ and of $C_{26}H_{20}O_4$ (C—78.69, H—5.05) are so small, and the properties of the described substances so much alike, that further proof of their non-identity is absolutely necessary.

The second substance formed in the action of acids on the white resin remained in the residue after extraction with alcohol, and was obtained pure by boiling out with a very large amount of alcohol. It is but slightly soluble in hot alcohol; one litre of alcohol dissolving about 0.15 gram of substance, which separated on cooling in white needles. The yield obtained of this substance is small.

The intensity of the action of benzoic aldehyde on resorcin depends largely on the acid used. While chlorhydric and sulphuric acids cause a rise of temperature to 55–60°, phosphoric acid induces a much slower reaction, and the temperature of the alcoholic solution only rises to 35–40°. Organic acids are still slower in causing the reaction. The following experiments were made with a solution of three parts of absolute alcohol, one part of resorcin and aldehyde.

Two drops glacial acetic acid were added. A rise of temperature did not take place. The crystalline substance began to form after several days standing, but the liquid still contained unchanged benzoic aldehyde. After four days a considerable precipitate was deposited and the solution contained nothing but the white resin.

Three grams of glacial acetic acid. The reaction proceeded very slowly. A deposit began to be formed after standing two days, and the aldehyde and resorcin were not completely converted into the resin until the mixture had stood for a week.

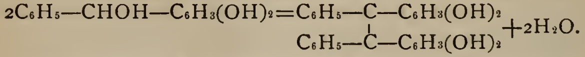
Two drops formic acid. No rise in the temperature of the solution. The reaction was completed in two days. With lactic acid the result is similar.

One-half gram of oxalic acid. A precipitate was formed in 24 hours. It consisted principally of prisms, which appear to be more soluble in alcohol than the plates formed by chlorhydric acid.

Several preliminary experiments on the behavior of the aldehyde-resorcin mixture towards alkalies have been made. It is necessary to keep the solution as much as possible from the air, since the substances formed are rapidly oxidised in alkaline solutions. Caustic soda, potash and potassium carbonate, one-half gram of each, gave the same result. The solution took, after standing several hours, a brownish color. In 24 hours the substances were converted into the above-described, or a similar resin.

The action of aromatic aldehydes on phenols, in the presence of a small amount of acid, is to form an amorphous resin, but the facility with which this is formed depends on the nature of the phenol and aldehyde. In the cold a trace of chlorhydric acid caused no action between benzoic aldehyde and phenol in alcoholic solution, but several hours' heating sufficed to convert these substances quantitatively into a resin corresponding to the resorcin resin. The orcin mixture rose in temperature to 40–45°, while the pyrogallol mixture only reached 35–40° under the conditions that the resorcin mixture reached 55–60°. Similar results were obtained from salicylaldehyde and phenol. Although it is somewhat premature to discuss the constitution of the compounds formed, and the nature of the action of aldehydes on phenols, I wish to state briefly what appears, from our present knowledge, to be the most probable interpretation. Aromatic aldehydes and phenols are probably first converted, by carbon polymerisation, into oxy-carbinols by traces of mineral acids. Whether a trace or a large amount of acid is used it is probable that these compounds are the primary products of the reaction. The further action will depend on the presence of a dilute acid, or an excess of the phenol and an acid with a strong affinity for water. With a dilute acid a condensation takes place; a result which is in accordance with the properties of the aromatic oxy-carbinols of undergoing a similar condensation when heated with traces of a mineral acid. Thus o-p-dioxybenzophenone[1] and dipara-dioxybenzophenones,[2] under these conditions, pass over into compounds which are probably derivatives of ethylene. In presence of a concentrated acid and a phenol, a different reaction may take place. The elements of water are extracted with the formation of a derivative of triphenylmethane. That the action of dehydrating agents on mixtures of secondary aromatic carbinols and aromatic hydrocarbons is to form triphenylmethane derivatives has been shown in a number of instances. It is possible that Etti, who used a very large proportion of fuming chlorhydric acid, has obtained compounds from vanillin and phenols which are derivatives of triphenylmethane; but the difficulty of obtaining this class of compounds in a condition suitable for analysis, unless proper precautions are taken to exclude the air, and the fact that Baeyer under the same conditions obtained compounds belonging to the ethylene group, show that further proofs than analyses are necessary before any confidence can be placed in his conclusions. Etti has apparently based his conclusions largely on a generalisation of Baeyer,[3] which that chemist evidently intended to apply only to the action of fatty aldehydes on phenols in presence of certain dehydrating agents. The experiments described in the following note make it probable that fatty aldehydes act on phenols, in the presence of traces of mineral acids, in much the same way as aromatic aldehydes do.[4]

The action of heat, or dilute acids, on the benzaldehyde-resorcin resin may be represented as follows:



$$2C_6H_5{-}CHOH{-}C_6H_3(OH)_2 = \begin{array}{l} C_6H_5{-}C{-}C_6H_3(OH)_2 \\ \qquad\;\;\, | \\ C_6H_5{-}C{-}C_6H_3(OH)_2 \end{array} + 2H_2O.$$

This formula is in accordance with the existence of four hydroxyls and the compound taking up two hydrogen; but, as already stated, it cannot be considered other than as a suggestion.

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[1] This Journal, **5**, 89.

[2] Annalen der Chemie, **202**, 132.

[3] Berichte der deutschen chemischen Gesellschaft, **12**, 645.

[4] It is likely that the behavior of aldehydes towards resorcin in the presence of a trace of chlorhydric acid may be used as a test for that class of substances. Whether other groups of substance show the reaction will be made the subject of an examination. Of interest also will be the examination of the behavior of aldehydes towards aromatic hydrocarbons, and phthalic anhydride toward phenols, in the presence of a small quantity of a mineral acid.

Summary.

I. Mixtures of aromatic aldehydes and phenols are converted by mere traces of acids, more or less rapidly, according to the acid used, into white resins.

II. The resorcin-benzaldehyde resin is converted by the further action of dilute acids into two crystalline compounds, one of which is isomeric with the resin when the latter is dried at 100°.

III. Fixed alkalies and potassium carbonate convert a mixture of resorcin and benzoic aldehyde into a resin.

IV. The properties of the crystalline compound $C_{26}H_{20}O_4$ resemble those of the so-called crystallisable resins. From its alkaline solution it is precipitated by acids in the form of a resin, which separates in form of the original crystals from the alcoholic solution.

V. The above results make it extremely probable that the formation of at least some of the resins in the vegetable world is due to aldehydes and phenols coming in contact with the contents of the cells, as both of these classes of compounds are undoubtedly among the products formed in plant-life.

TUFTS COLLEGE, MASS , *July* 3, 1883.

II.

BY A. MICHAEL AND A. M. COMEY.

The following experiments on the action of alkylaldehydes on phenols are considered as preliminary work of an investigation of the reaction in the manner stated in the preceding paper.

Action of Ethylaldehyde on Orcin and Resorcin.

A drop of chlorhydric acid added to a mixture of aldehyde and orcin causes no change in the cold; but when the solution is heated for a moment at 100°, a copious white precipitate is deposited. For the preparation of the substance, equal weights of aldehyde and orcin were dissolved in eight parts of absolute alcohol, and three drops concentrated chlorhydric acid added. The precipitate, formed on heating the solution for a minute at 100°, was filtered, washed out well with alcohol and then with water. For analysis it was dried at 100° in a current of CO_2.

0.190 gram of substance gave 0.5035 gram of CO_2 and 0.1240 gram of H_2O.

	Theory for $C_{18}H_{20}O_4$.	Found.
C	72.00	72.26
H	6.67	7.24

The substance has a slight yellowish color, and consists of small round plates. It is stable in the air at ordinary room-temperature; at 100° it rapidly takes a dark color. The usual organic solvents dissolve it neither in the cold nor in the heat. In alkalies it dissolves to form a solution that rapidly oxidises in the air. Although the formation of this substance may be represented by the general equation representing the action of aromatic aldehydes on phenols, its properties indicate that it has a more complicated constitution than the members of that class of substances:

$$2CH_3—CHO + 2\,C_6H_3(OH)_2CH_3 = C_{18}H_{20}O_4 + 2H_2O.$$

The action of ethylaldehyde on resorcin is similar to its action on orcin. A solution of equal parts of aldehyde and resorcin dissolved in three parts of alcohol, and several drops of chlorhydric acid, solidified on heating at 100° to a gelatinous mass. It was pressed out between bibulous paper, and then extracted with boiling alcohol. The substance is insoluble in the usual solvents. Heated to a high temperature it takes fire and burns like tinder. We were unable to obtain it in a state suitable for analysis, as it decomposed in a current of CO_2 at 100°.

Action of Chloralhydrate on Resorcin.

When an aqueous solution of chloralhydrate and resorcin is boiled in a flask connected with an inverted cooler, it gradually takes a darker color, and after some hours a crystalline precipitate begins to settle. We found that working according to the following directions gave the best yield: Five parts of the hydrate, ten parts of resorcin, and forty parts of water were heated for 12–24 hours in a flask connected with an inverted cooler. The light yellow crystalline product of the reaction separated in part from the boiling solution, and a further quantity on cooling; sometimes, however, not until the sides of the vessel were rubbed with a glass rod. A portion of the filtrate gave a copious precipitate of silver chloride on addition of silver nitrate, and the remainder yielded on continued boiling a second precipitate of the substance. From the amounts taken, about 2½ grams of the new substance were obtained. For analysis it was recrystallised several times from dilute alcohol, and care was taken to avoid unnecessary heating in contact with the air. The substance does not contain chlorine. The analyses gave the following numbers:

I. 0.2418 gram of substance, dried *in vacuo*, gave 0.5632 gram of CO_2 and 0.0878 gram of H_2O.

II. 0.2632 gram of substance, dried *in vacuo*, gave 0.6170 gram of CO_2 and 0.1078 gram of H_2O.

III. 0.2393 gram of substance, dried *in vacuo*, gave 0.5600 gram of CO_2 and 0.0938 gram of H_2O.

	Theory for $C_8H_6O_3$.	Found.		
		I.	II.	III.
C	64.00	63.53	63.93	63.82
H	4.00	4.03	4.54	4.35

The substance dried in a vacuum does not contain water of crystallisation; the air-dried compound did not lose in weight when heated in dry CO_2 at 100°. It separates from a solution in very dilute alcohol on cooling as fine, yellowish needles, which melt under decomposition at a high temperature. They are somewhat soluble in hot water, more easily in a boiling aqueous solution of resorcin, and are deposited on cooling as prismatic needles. In alcohol and acetic acid they are extremely soluble in the heat, moderately in the cold. The substance is very sensitive to the action of oxygen. It is, when pure, probably perfectly white; but exposure to the air for a few moments suffices to give it a yellowish tint. It dissolves in concentrated sulphuric acid, and the solution takes a beautiful blue color on exposure to the air. Alkalies dissolve it readily in the cold; the solution becomes brown almost immediately on exposure to the air, owing to the absorption of oxygen. After treatment of its alcoholic solution with nascent hydrogen the addition of water gave an almost white precipitate. This precipitate on drying, or when recrystallised, took a yellowish tint. A reduction had not taken place. This was proven by converting it into the acetyl derivative, and a comparison of its properties with those of the acetyl derivative of the original compound. These experiments make it probable that the product analysed was slightly oxidised. The substance is completely oxidised in the cold by potassium permanganate to carbon dioxide. An attempt was made, by adding a small quantity of permanganate at a time, to effect the isolation of intermediate products, but it was found that part of the substance was completely oxidised while the rest remained unchanged.

To prepare the acetyl derivative 2 grams of the substance, 4 grams of acetic anhydride, and 1 gram of fused sodium acetate were heated for several hours at 100°. The solid substance dissolved on heating in the anhydride, and soon a separation of the new product began. The product of the reaction was extracted with water, and the residue crystallised several times from strong alcohol. On analysis the following numbers were obtained:

I. 0.2302 gram of substance, dried at 100°, gave 0.5210 gram of CO_2 and 0.0895 gram of H_2O.

II. 0.2350 gram of substance, dried at 100°, gave 0.5317 gram of CO_2 and 0.0988 gram of H_2O.

III. 0.2227 gram of substance, dried at 100°, gave 0.5065 gram of CO_2 and 0.0905 gram of H_2O.

	Theory for $C_8O_3H_4(OCCH_3)_2$.	Found.		
		I.	II.	III.
C	61.53	61.71	61.70	61.20
H	4.27	4.32	4.67	4.51

The compound separates from alcohol as white, prismatic crystals that melt at 159°. It is insoluble in hot water, moderately soluble in hot alcohol, but slightly in cold. In alkalies it is insoluble in the cold; when heated a gradual solution was effected. The substance is very stable towards oxygen, and may be heated in the air to 120° without undergoing any change. Its stability indicates that the instability of the mother-substance towards oxygen is due to oxidation beginning at its hydroxyl.

The chloral-resorcin compound can be heated with benzoylchloride to 100° without a reaction ensuing; at 120° an evolution of chlorhydric acid begins. A mixture of the substance and benzoylchloride, in proportion of one mol. to five, was heated at 120° until the disengagement of chlorhydric acid ceased. The product of the reaction was boiled out several times with water, and the insoluble residue crystallised four times from alcohol. An analysis gave the following numbers:

0.2158 gram of substance, dried at 100°, gave 0.5827 gram of CO_2 and .0868 gram of H_2O.

	Theory for $C_8O_3H_4(OCC_6H_5)_2$.	Found.
C	73.74	73.62
H	3.91	4.47

The substance separates from alcohol as small crystals, which have a slight pinkish tint. They melt at 165°. In boiling water they are insoluble, moderately soluble in hot alcohol, nearly insoluble in cold.

The formation of the compound $C_8O_3H_6$ from chloralhydrate and resorcin may be represented by the following equation:

$$C_6H_4(OH)_2 + 2CCl_3—CH(OH)_2 \\ = C_8H_6O_3 + CCl_3COOH + 3HCl + H_2O$$

The examination of the substance is not sufficiently advanced to allow an insight into its constitution, more than as follows from the experiments on the action of acetic anhydride and benzoylchloride, that it contains two hydroxyl. We consider it useless, under these circumstances, to offer any suggestion regarding its constitution, but reserve the right to return to the subject later in the investigation. Chloralhydrate and orcin yield a similar compound, melting at 250°, whose acetyl derivative melts at 190°. This compound is more stable towards oxygen than the resorcin compound. It is probable that corresponding derivatives of other phenols can be obtained in a similar manner.

TUFTS COLLEGE, MASS., *July* 5, 1883.

LABORATORY NOTES.—III.[1]

BY ARTHUR MICHAEL.

X.—SOME CONVENIENT QUANTITATIVE LECTURE APPARATUS.

The need felt by teachers of chemistry not only to present to their hearers the principal facts of their science qualitatively, but also quantitatively, has been the cause of what may be called an evolution in lecture apparatus. This has culminated in instruments, notably by Bunsen and A. W. Hofmann, which are hardly open to improvement as far as simplicity combined with accuracy are concerned. Their deficiency is more in expensiveness, and, especially in regard to Hofmann's apparatus, fragility. In this note some quantitative lecture apparatus will be described, which were devised with the special view of combining sufficient accuracy with stability and cheapness. It is becoming more and more desirable that all students of chemistry should convince themselves of the truth of the most important reactions, and the composition of some of the principal inorganic compounds, from personal observation, and apparatus has become imperative which can be made by any one having a slight experience in glass-blowing. The aid that a knowledge of glass-blowing affords to a scientific chemist cannot be overestimated. The writer is convinced that a training in it should never be omitted from the course required of students making chemistry their profession.

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[1] This Journal, **1**, 413; **5**, 192.

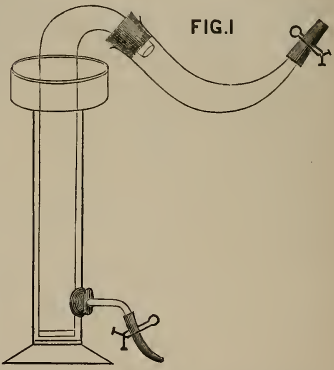

FIG. I

The trough used is Liebig's well-known instrument slightly modified. Liebig's trough has notably two defects. The eudiometer after the explosion is apt to bump, which often causes an overflow of mercury, and even at times breaking the apparatus. This is remedied by placing a rubber plug on the bottom of the trough, and holding the eudiometer firmly down on it by means of a retort-clamp. A second defect is in the difficulty of emptying, or adjusting the height of the mercury, even when it does not contain a eudiometer. To obviate this inconvenience a tubulus is brought on the narrow part of the trough, an inch or two above the foot, and fitting into it a cork with a tube bent at right angles and ending in a piece of rubber tubing and spring-clamp[1] (Fig. 1). The cup of the trough should be three or four inches in diameter, while the narrow part need not be much wider than the largest eudiometer in use. These additions, as slight as they may seem, quite change the apparatus in respect to convenience and handiness.

The eudiometers should be several inches higher than the trough, and may be conveniently divided by calibration into twelve equal divisions. In order to render the readings noticeable from a distance, rings of dark rubber are placed over each division. A rubber band, about one-half inch in width, brought over the open end of the eudiometer, will be found to render it less liable to breakage, and is also of use in indicating the proximity of the open end to the surface of the mercury. To obviate the necessity of lowering the eudiometer a number of times while introducing a given volume of gas, it has been found desirable that each instrument should have a second calibration, which is made by introducing successively a unit volume of air, when the eudiometer is held upright, with the upper end of the broad rubber band level with the mercury in the trough. The results are marked in half-lines across the instrument, with the number of unit volumes.

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[1] A hole drilled by means of a diamond and fitted with a cork and tube will answer the purpose. The described trough, as well as the other apparatus which will be mentioned, can be obtained of the Prang Educational Company, No. 7 Park Street, Boston, Mass.

In the analysis of gases requiring an absorption of part of the products formed by the explosion a modified eudiometer is used, which obviates the introduction of liquid reagents. The instrument ends in a tube bent in the form of a half-circle, and connected by a rubber tube with a small bulb (Fig. 2). After the explosion, the communication between the eudiometer and the bulb containing the absorption-liquid is opened, and the eudiometer sunk to the bottom of the trough. Owing to the gases being under pressure, the absorption takes place quite rapidly, and is generally finished in one-half to three-quarters of an hour, when the spring-clamp is closed and a second reading taken. The instrument has the further advantage of permitting the examination of the absorption liquid.

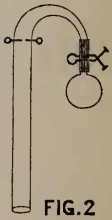

FIG. 2

Bunsen[1] has devised a very ingenious apparatus for the purpose of ascertaining the composition of certain oxides by measuring the volume of oxygen used in oxidising a known weight of the element. The following apparatus involves the principle of Bunsen's, but is much more compendious and needs less mercury, without a very great loss in the accuracy of the results. A tube about an inch longer than the trough is graduated, beginning an inch and a-half from the upper end, into about 160–180 parts of 1 cc. each. The upper end of the measuring tube is joined to a tube of about three-fourths of its diameter, and bent to form an angle of 45°. This tube is connected by a rubber cork with a curved tube of difficultly fusible combustion tubing, which is drawn out at the other end to a small tube, and closed by a piece of tubing and spring-clamp (Fig. 1).

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[1] See Heumann, Anleitung zum Experimentiren bei Vorlesungen über anorganische Chemie, 52.

In the analysis of sulphur and carbon dioxides, when the volume of the gas after the combustion remains unchanged, the apparatus is about half filled with oxygen. This is done by connecting the open end of the heating-tube with an oxygen generator, displacing the air, then the measuring-tube brought under mercury to 100 cc., the generator disconnected and the heating-tube closed. By heating the carbon or sulphur, which is previously placed in the heating-tube—the first, to prevent the tube from cracking on a piece of platinum foil, the latter on a chip of glass—a vivid combustion takes place, which can be seen from a distance. In the analyses of oxides, when the volume after combustion is less than the volume of oxygen taken, the measuring-tube is filled with oxygen to about 20 cc. from the open end, and a quantity of the element used which requires from 100 to 120 cc. of oxygen for its combustion. Before heating the substance, the measuring-tube is firmly placed on the rubber plug of the trough, which is then filled with mercury. The results obtained in the analyses of phosphorus pentoxide,[1] arsenic trioxide, magnesium oxide, &c., are sufficiently accurate to prove the constitution of these compounds beyond a doubt.

Bunsen's apparatus has hitherto only been used in ascertaining the volume of oxygen required for the combustion of certain elements. The above-described apparatus, or a slight modification of it, can be used for ascertaining the composition of a large number of important inorganic compounds, by measuring the volume of gas evolved in the decomposition of a known weight.

In studying quantitatively the decomposition of a substance, potassium chlorate for instance, by heat, a weight of it which will give off about 120 cc. of gas is placed on a small platinum boat and brought into the heating-tube. After the mercury is adjusted opposite the zero mark, the substance is heated by a Bunsen burner until the volume of gas in the measuring-tube remains constant, when, after cooling, a second reading will give the volume of gas evolved in the reaction.[2]

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[1] Amorphous phosphorus must, of course, be used in this experiment. The commercial product leaves an ash, which is insoluble in water. It is therefore necessary to purify it, or determine the ash and make the required correction.

[2] It is well to add a trace of platinum black in the analysis of $KClO_3$. A much smaller heating tube closed at one end, and the bent open end fitted into the measuring tube, is advantageously used in such pyro-analyses. That the measuring tube and trough can be replaced by an apparatus constructed on the U tube principle is evident.

For the purpose of estimating the volume of a gas given off in a wet reaction, the heating-tube is replaced by a small flask of a capacity of 20–30 cc., and connected by a tube, attached to the neck and bent at right angles, to a drying tube. Through a rubber cork in the flask, a glass rod bearing a small perforated platinum basket and marked when the basket is in the upper part of the flask, is brought, and the rod greased that it may be freely moved in the cork. The drying tube is filled with calcium chloride, and connected by a rubber cork with the measuring-tube (Fig. 3). If the gas is soluble in the liquid used for decomposition, the flask is replaced by a small test-tube, on which a mark is brought showing that two or three cc. of the liquid are used, and a correction made for solubility. For analysis the flask is half-filled with the liquid, the glass rod pressed down until the mark is in contact with the upper end of the cork; and after the volume of air in the measuring-tube is read, the basket, containing a weighed quantity of the substance, is brought under the liquid. After the reaction is over the rod is brought back to the original position, and from a second reading the volume of gas evolved is ascertained.

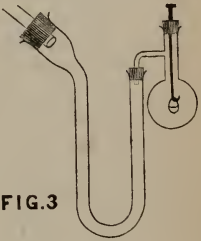

FIG. 3

I have not entered into the details of handling the apparatus, because they do not essentially differ from those necessary in using an ordinary eudiometer. Before each reading, the mercury in and outside the measuring-tube is brought to a level, and barometric and thermal observations are, of course, necessary. It is evident that three classes of reactions may be quantitatively examined by means of the apparatus. Firstly, those depending on a volume of oxygen absorbed;[1] secondly, those in which a gas is evolved at the temperature under a red heat; and, finally, those reactions in which a gas is evolved in the action of a liquid on a solid. The important reactions which can be examined in the apparatus are so numerous that its range is hardly exceeded by any other lecture apparatus. In most cases the complete analysis may be realised in a few moments by a volumetric analysis of the product

[1] No experiments have been made as yet on reduction of heavy metallic oxides in hydrogen, under similar conditions; but I do not doubt that sufficiently accurate results would be obtained.

remaining in the heating-tube or decomposition flask. Thus, in the analysis of potassium chlorate, the chloride remaining in the heating-tube can be washed into a beaker and a volumetric chlorine estimation made; or, in the investigation of the action of chlorhydric acid on metallic zinc or calcium carbonate, a known volume of standard acid taken and the undecomposed acid determined by titration.

It is often desirable to keep a small volume of a gas for subsequent investigation—a purpose for which the following simple gasometer has been found useful: Two small bottles, of about 50 cc. each, are fitted with double-bored rubber corks, and connected by a glass tube bent in the form of a syphon. The limb of the syphon, which is in the flask used as gasometer, is somewhat longer than the other limb. Through the second hole of that bottle a bent delivery tube, provided with a small glass stopcock, barely passes, and a small bent tube passes through the cork of the second bottle. For use, the gasometer and syphon are filled with mercury, and the end of the delivery tube then connected with the generating flask.[1] A small quantity of mercury is allowed to remain in the gasometer. The apparatus works, to a certain extent, automatically. On opening the stopcock of the charged gasometer, mercury will pass over until it is on a level in both bottles, and the remaining half can be expelled by applying pressure to the bent tube of the second bottle. A well-constructed apparatus will keep a gas for weeks without an appreciable change.

I wish finally to call attention to a slight modification of Hofmann's well-known V tube, which permits the collection of both the products of decomposition, and can, therefore, be used for quantitative analysis. On the upper side of the bend of the tube a glass tube is connected, which is an inch higher than the limbs of the V tube (Fig. 4). The limbs are graduated in five or six equal parts; those on the open limb beginning, not at the open end, but about one half an inch from it. For use, the apparatus is filled with liquid, and the cork, through which a glass

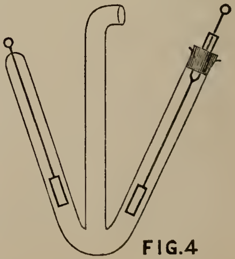

FIG. 4

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[1] A more advantageous form is to have the delivery tube connected to the neck of the gasometer, directly under the rubber cork.

tube with platinum electrode passes, is pressed into the open limb until it reaches the first graduation. The displaced liquid flows out through the middle limb, which is conveniently connected with a rubber tube. Ungraduated Ure's eudiometers, provided with a short horizontal tube on the lower side of the bend, or on the upper side and bent downwards, make a cheap and efficient substitute for Hofmann's lecture-eudiometer, especially for students' use in the laboratory.

XI.—OBSERVATIONS ON THE ACTION OF ACETYLCHLORIDE AND ACETIC ANHYDRIDE ON CORN AND WHEAT STARCH.

The following preliminary experiments on the action of acetic anhydride and acetylchloride on corn and wheat starch were made with a view of ascertaining whether the typical physical differences of these varieties of starch are noticeable in their acetyl derivatives. According to Schützenberger,[1] starch heated with acetic anhydride at 140° yields an amorphous triacetyl derivative.

I. Two grams (1 mol.) of potato starch and 5 grams (4 mols.) of acetic anhydride were heated in a closed tube at 148–152° for two hours. The starch was converted into the acetyl derivative. It did not give a coloration with iodine solution; but after boiling with alkaline solutions it gave the blue starch test, showing that starch was regenerated. The granules, under the microscope, could not be distinguished from the original potato granule. The acetyl compound is insoluble in acetic acid, but on continued boiling a gradual solution is effected. The addition of water precipitates an amorphous white substance, which is soluble in hot alcohol and cold acetic acid.

A second tube prepared like the first with the difference that corn starch was used, was also heated for two hours at 148–152°. The properties of this acetyl derivative are like those of corresponding derivative of the potato granule, but it had the form of the corn granule. It is evident from these experiments that the characteristic forms of the potato and corn granules are not changed when these starch-varieties are acetylised.

II. Two tubes were prepared like the above, excepting that anhydride containing 10 per cent. of acetic acid was used, and heated at

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[1] Ann Chim. Phys. [4], **21**, 235.

158–160°. The granules of acetyl corn starch appeared somewhat flattened and were not sharply defined. They still retained, however, the general appearance of the corn granule. The granules of acetyl potato starch retained their sharp contour; but were, perhaps, slightly enlarged. After heating with water they appeared flattened and lost their well-defined form.

III. Two grams of corn starch and five grams of acetylchloride were heated for fifteen hours at 55–58°. The tube on opening gave off a considerable quantity of chlorhydric acid. Continued heating did not cause a further formation of chlorhydric acid. The contents of the tube was extracted with chloroform, filtered from insoluble, undecomposed starch, and the chloroform of the filtrate driven off by heating on a water-bath. The residue was then dissolved in alcohol, treated with bone black, and gave on cooling a grayish white precipitate, which melted at 144°. Redissolved in warm, dilute alcohol, a white amorphous substance separated on cooling, which began to soften at 148°, and had the constant melting-point of 150–151°. The first alcoholic filtrate gave on concentration no further precipitate, but on addition of water a white amorphous substance separated, which on crystallisation from very dilute alcohol gave a substance sinking together at 126°, and melting at 128–129°. Acetylchloride has evidently quite a different action on starch than acetic anhydride. The substance melting at 150° is probably not an acetyl derivative of starch, but of one of the dextrine modifications. The substance melting at 129° is very likely formed secondarily by the action of hot alcohol on the first product. A second tube prepared as the above, but on the treatment of its contents, unnecessary heating with alcohol and boneblack avoided, gave only a trace of the product melting at 129°.

A tube containing potato instead of corn starch, and subjected to the same conditions, gave similar results. A slight difference in the properties of the acetylised compound is noticeable, but I do not think that they warrant a conclusion as to chemical differences in the properties of the two products. The substance had a slight brown color, and, sinking together at 145°, melted at 146–148°.

TUFTS COLLEGE, MASS., *July 16th*, 1883.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

By Wolcott Gibbs, M. D.

Rumford Professor in Harvard University.

[Continued from Vol. 3, p. 416.]

The compounds which I have hitherto described may be embraced under the general formula—

$$mRO_3.2R'_2O_5.pR''_2O,$$

in which m may represent any even number from 10 to 48 inclusive, p the number of molecules of base (old style), R an atom of tungsten or molybdenum, and R′ one of phosphorus or arsenic. I shall now proceed to show that these results may be generalised in a variety of different ways, and, further, that there are other typical formulas, perhaps less general than that above given, but still embracing many interesting and instructive special cases.

HYPOPHOSPHO-MOLYBDATES.

Hypophospho-molybdate of Ammonium.—When solutions of 14:6 acid ammonic molybdate and sodic hypophosphite are mixed, no precipitate is formed, but the liquid takes a fine blue color from the partial reduction of molybdic teroxide to Mo_2O_5. On addition of chlorhydric acid and stirring for a short time, a large quantity of a crystalline salt separates. This is to be filtered off, well drained by the filter-pump, and washed with cold water, in which it is not very soluble. When perfectly pure and free from Mo_2O_5 the salt presents colorless prismatic crystals, which are readily soluble in hot water. The solution, at first pale blue, speedily assumes a deeper tint; with cold water a colorless strongly acid solution may be obtained, and with such the reactions here given were obtained. Baric chloride gives no precipitate alone, but after adding ammonia a colorless salt is thrown down, which is at first flocky, but which soon becomes fine-grained granular-crystalline. Strontic and calcic chlorides behave in a similar manner, but the calcic precipitate does not form so rapidly. Manganous sulphate gives no precipitate alone, but after adding ammonia a white flocky salt is formed, which becomes yellowish on standing. Cupric sulphate behaves in the same manner; the precipitate after the addition of ammonia is green and flocky. The mixture with solution of copper is not reduced on boiling, either alone or after addition of chlorhydric acid. The solution of the hypophospho-molybdate gives a canary-yellow precipitate with mercurous nitrate, and a nearly white precipitate with argentic nitrate, which soon becomes gray and finally black. Thallous nitrate gives a white flocky precipitate. When the dry salt is heated, it becomes at first black and fumes slightly, but on further heating it melts to a dark blue mass which gives off a little molybdic teroxide on heating to redness. The fused mass dissolves readily in hot water, forming a deep blue solution which has an acid reaction, and gives with magnesia-mixture the characteristic ammonio-magnesic phosphate. The effect of heat is represented by the equation

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[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

$$8MoO_3.2[H_2.PO.OH].2(NH_4)_2O + 2H_2O = \\ 8MoO_3 + P_2O_5 + 3H_2 + 2(NH_4)_2O + H_2O.$$

In the analyses the loss by ignition corresponds to $2(NH_4)_2O + H_2O + 3H_2$, and the residual mass to $8MoO_3 + P_2O_5$, when the ignition is made with sodic tungstate. In this salt—

1.3172 gram lost on ignition with WO_4Na_2 0.1329 gram = 10.09 per cent. H_2O, $(NH_3)_2O$, and H.

1.0764 gram lost on ignition with WO_4Na_2 0.1086 gram = 10.09 per cent. H_2O, NH_3, and H.

1.2369 gram gave 0.1836 gram NH_4Cl = 7.21 per cent. $(NH_4)_2O$.

1.2850 gram gave 0.0918 gram $(NH_4)_2O$ by titration = 7.15 per cent. $(NH_4)_2O$.

2.4322 grams gave 0.3860 gram $P_2O_7Mg_2$ = 9.42 per cent. PO_2H_3.

1.6217 gram gave 0.2578 gram $P_2O_7Mg_2$ = 9.30 per cent. PO_2H_3.

The analyses lead to the formula

$$8MoO_3.2[H_2.PO.OH]2(NH_4)_2O + 2Aq,$$

which requires:

		Calc'd.	Mean.	Found.	
$8MoO_3$	1152	80.89	80.97	...	...
$2PO_2H_3$	132	9.27	9.36	9.42	9.30
$2(NH_4)_2O$	104	7.31	7.18	7.21	7.15
$2H_2O$	36	2.53	2.49	2.47	2.52
	1424	100.00	100.00		

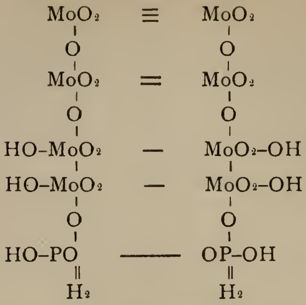
In computing the results of the analyses the loss of weight by ignition, 10.09 per cent., is of course taken to represent $2(NH_4)_2O + H_2O + 3H_2$, in accordance with the equation given above. In the analyses the quantity of hypophosphorous acid was determined by dissolving the salt in a solution of sodic carbonate, and then adding bromine, which with the aid of heat readily converts the hypophosphorous into phosphoric acid. The quantity of the former could not be determined by means of potassic hypermanganate in an acid solution. Bromine does not act sensibly upon acid solutions, and even an excess of nitric acid effects an imperfect oxidation. These facts, taken in connection with the relations of the salt to solutions of copper and silver, seem to show that the stability of hypophosphorous acid is increased by its combination with molybdic teroxide. The salt has, as stated, a strong acid reaction, and the limit of the basicity of this class of compounds still remains to be determined. The formula may also be written:

$$8MoO_3.2[H_2.PO.(NH_4O)_2]2H_2O + 2Aq.$$

The constitution of hypophosphorous acid was first established by Würtz. More recent investigations in organic chemistry have shown that it is to be regarded as dihydryl-phosphinic acid, and that it forms the initial term and type of an extensive series of organic acids, in which the two atoms of hydrogen attached to the phosphorus are replaced by methyl, phenyl, &c., and in which also arsenic may replace phosphorus. I do not propose at present to proceed further in this particular line of research, but will content myself with the statement that a solution of dimethyl-arsinic (cacodylic) acid gives immediately in one of 14:6 acid ammonic molybdate a beautiful colorless crystalline precipitate. It can hardly be doubted that this is a dimethyl-arsino-molybdate belonging to the general type represented by the formula

$$mMoO_3.2[(CH_3)_2.AsO.(OH)]n(NH_4)_2O.$$

The structural formula of the hypophospho-molybdate above described, or rather of the corresponding acid, may be written, in accordance with the general principles already assumed, as follows:



$$\begin{array}{ccc}
MoO_2 & \equiv & MoO_2 \\
| & & | \\
O & & O \\
| & & | \\
MoO_2 & = & MoO_2 \\
| & & | \\
O & & O \\
| & & | \\
HO\text{–}MoO_2 & — & MoO_2\text{–}OH \\
| & & | \\
HO\text{–}MoO_2 & — & MoO_2\text{–}OH \\
| & & | \\
O & & O \\
| & & | \\
HO\text{–}PO & \text{———} & OP\text{–}OH \\
\| & & \| \\
H_2 & & H_2
\end{array}$$

In this formula the acid is supposed to correspond to the ammonium salt described.

HYPOPHOSPHO-TUNGSTATES.

The salts of this series are not very well defined as regards their physical properties, and it is difficult to obtain any single one in a state of perfect purity. They are most readily prepared by boiling acid tungstates with a solution of hypophosphorous acid, and appear to be in general very soluble in water, yielding sometimes thick syrupy liquids, and sometimes gelatinous masses more or less colored by the partial reduction of tungstic teroxide.

Potassic Salt.—When a strong solution of hypophosphorous acid is mixed with one of 12 : 5 acid sodic tungstate, the liquid becomes turbid and yellowish, and after a short time gelatinises to a pale yellow mass. This is to be dissolved in boiling water, and a solution of potassic bromide added, which after a short time gives a white crystalline precipitate, to be drained upon the filter-pump, redissolved in hot water, again crystallised, drained, washed with cold water, and dried on woollen paper. As thus prepared, the salt presented small colorless granular crystals, soluble in hot water to a somewhat turbid strongly acid liquid, which effervesced with alkaline carbonates. The solution gave no precipitate with cupric sulphate, and no copper was reduced on boiling either with or without chlorhydric acid. Argentic nitrate gave a turbid white solution; on boiling, silver was reduced. Mercurous nitrate gave a white flocky precipitate, which on boiling became yellow, and finally dirty greenish yellow, without reduction of mercury. Baric chloride gave a white precipitate of indistinct feathery crystals. When heated in a porcelain crucible the salt became blue, and finally white, giving off a sharp acid smell. The residue dissolved in water, in part at least, forming a strongly acid solution. Of this salt—

1.2295 gram lost on ignition 0.0340 gram = 2.76 per cent. water and hydrogen.

1.2295 gram gave 1.1172 gram $WO_3 + P_2O_5$ = 90.84 per cent.

0.7272 gram lost on ignition with WO_4Na_2 0.0203 gram = 2.79 per cent.

1.5110 gram gave 0.1921 gram $P_2O_7Mg_2$ = 7.57 per cent. PO_2H_3.

The analyses lead to the formula

$$18WO_3.6[H_2.PO.OH]4K_2O + 7Aq,$$

which requires:

		Calculated.		Found.	
$18WO_3$	4176	82.31	90.11	82.71	90.28
$6PO_2H_3$	396	7.80		7.57	
$4K_2O$	376	7.41		7.42	
$7H_2O$	126	2.48		2.45	
	5074	100.00		100.15	

In the analysis the hypophosphorous acid was determined by oxidation with bromine in an alkaline solution and precipitation with magnesia-mixture. The formula given may be written, with equal probability,

$$18WO_3.6[H_2.PO.OK]K_2O.3H_2O + 7Aq,$$

since the assignment of the fixed base is purely arbitrary; other arrangements are also possible. I am disposed to regard the salt as acid, with the formula

$$2(6WO_3.2[H_2.PO.OH]2K_2O) + 6WO_3.2[H_2.PO.OH]2H_2O + 5Aq,$$

so that the type of the corresponding acid, setting aside the question of basicity, will be

$$6WO_3.2[H_2.PO.OH]2H_2O.$$

The structural formula of such an acid will be similar to that already given in the case of the hypophospho-molybdate described. Further investigation may, however, show that the more complex formula must be admitted. I content myself with proving that there is at least one class of hypophospho-tungstates. In computing the direct results of the analyses I have assumed that, as in the case of the corresponding molybdenum compounds, the complex $2[H_2.PO.OH]$ is oxidised to P_2O_5 wholly at the expense of two molecules of WO_3 reduced to W_2O_5, which last is then again oxidised to $2WO_3$ by heating in air. This assumption appears to be justified by the changes of color observed on heating the salt. The actual loss of weight observed then corresponds to water and hydrogen only, the percentage of hydrogen being calculated from that of $P_2O_4H_6$.

When tungstic hydrate in excess is boiled with a solution of sodic hypophosphite, it dissolves very readily, giving a pale blue solution which yields on evaporation a thick syrupy liquid. This solution gives precipitates with $BaCl_2$, NH_4Cl, and KBr, and will furnish a convenient starting-point for further investigation. It does not oxidise readily in the air, even after long standing. A solution of dimethyl-arsinic acid gives with one of 12:5 acid sodic tungstate a beautiful colorless crystalline precipitate. I have not studied this compound, from want of proper facilities for work of the kind. It will, I think, prove to be a dimethyl-arsino-tungstate, coming under the general formula

$$mWO_3.2[(CH_3)_2.AsO.OH]nNa_2O,$$

and we may reasonably expect an extensive series of analogous compounds, in which other radicals take the place of methyl.

PHOSPHOROSO-MOLYBDATES.

Since phosphorous acid is now to be regarded as hydryl-phosphinic acid with the formula

$$[H.PO.(OH)_2],$$

the existence of a class of phosphoroso-molybdates and of phosphoroso-tungstates appeared, to say the least, a probable inference from that of the hypophospho-compounds already described.

Phosphoroso-molybdate of Ammonium.—When a solution of phosphorous acid—as prepared by the reaction of phosphorous chloride with water—is added to one of 14:6 acid ammonic molybdate, a very pale yellow indistinctly crystalline precipitate is formed, which is insoluble in cold water. Hot water dissolves it only in a small proportion, but gives a milky emulsion, which settles very slowly. For analysis the salt was drained on a filter-pump, well washed with cold water, and finally dried on woollen paper. Of this salt—

1.9695 gram gave 0.0980 gram $(NH_4)_2O = 4.97$ per cent. by titration.

1.1425 gram gave 0.0559 gram $(NH_4)_2O = 4.89$ per cent. by titration.

0.9301 gram lost on ignition with WO_4Na_2 0.1225 gram $= 13.17$ per cent.

1.2722 gram gave 0.1374 gram $P_2O_7Mg_2 = 7.97$ per cent. PO_3H_3.

The analyses correspond fairly well with the formula

$$24MoO_3.4[H.PO.(OH)_2]4(NH_4)_2O + 17Aq,$$

which requires:

	Calculated.		Found.	
$24MoO_3$	80.41	88.04	79.88	87.85
$4PO_3H_3$	7.63		7.97	
$4(MH_4)_2O$	4.84		4.89	4.97
$17H_2O$	7.12		7.22	
	100.00			

The salt certainly contained a little phospho-molybdate, to which the faint yellow tint was probably due. It is very difficult to obtain a solution of phosphorous which is absolutely free from phosphoric acid. With respect to the formula I remark that the number of molecules of water may be purely accidental, and that there is at present no sufficient reason for rejecting the simpler expression—

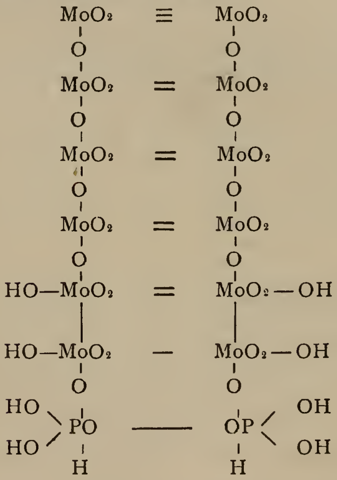
$$12MoO_3.2[H.PO.(OH)_2]2(NH_4)_2O + x Aq.$$

The type of the acid is then

$$12MoO_3.2[H.PO.(OH)_2]2H_2O.$$

A solution of baric chloride boiled with the phosphoroso-molybdate decomposes it more or less completely, giving a white very fine-grained crystalline salt. Under the same circumstances argentic nitrate gives a nearly colorless flocky substance, which quickly becomes darker, and finally assumes a dull violet color. Mercurous nitrate yields a clear pale yellow flocky salt; the phosphoroso-molybdate does not reduce a solution of mercuric chloride even on boiling. Cupric sulphate dissolves the salt to a clear blue liquid. Manganous sulphate also dissolves it, forming a colorless solution. Alkaline hydrates dissolve it very readily to colorless liquids. The salt is readily decomposed by heating in a porcelain crucible, and fuses at a low red heat, giving off vapors of molybdic teroxide. The fused mass on cooling is bluish gray. It dissolves readily in water to a deep blue liquid, which has a strongly acid reaction, and gives with magnesia mixture the reaction for phosphoric acid.

The structural formula of the acid corresponding to the ammonium salt may be written provisionally:



If we accept the views now generally received as to the constitution of hypophosphorous and phosphorous acids, the hypophosphomolybdates, hypophospho-tungstates, and phosphoroso-molybdates furnish a much needed demonstration of the fact, that in this whole class of compounds part at least of the hydroxyl is united to phosphorus directly, and a part only to tungsten or molybdenum. This will appear at once from the formulas for the two acids, since these cannot be broken up into simpler expressions,

$$[H_2.PO.OH], \quad \text{and} \quad [H.PO.(OH)_2],$$

or from the structural formulas which I have given. I shall return to this point hereafter, and give additional proofs of the twofold mode of combination of hydroxyl.

Further investigation will almost certainly show that the homologues of hydryl-phosphinic or phosphorous acid will also form complex acids with tungstic and molybdic teroxides. Thus methylphosphinic acid $[CH_3.PO.(OH)_2]$ should form at least one series of each of the general types:

$$mMoO_3.[CH_3.PO.(OH)_2]nH_2O.$$
$$nWO_3.[CH_3.PO.(OH)_2]pH_2O.$$

In these cases arsenic, and perhaps antimony, may replace phosphorus. Phosphoroso-tungstates may be formed by the action of phosphorous acid upon acid tungstates. The only salt obtained at present appears to have the formula

$$12WO_3.2[H.PO.(OH)_2]2K_2O + 12Aq.$$

I propose to return to this special point when describing the related groups of arsenoso-tungstates and antimonoso-tungstates and the corresponding molybdates. In the analysis of the phosphoroso-molybdate of ammonium the phosphorous acid was determined by dissolving the salt in an excess of a solution of sodic carbonate, oxidising with bromine, and precipitating with magnesia mixture.

VANADIO-MOLYBDATES.

The general analogy between vanadic, arsenic, and phosphoric pentoxides suggested to me the possibility of forming series of vanadio-molybdates and vanadio-tungstates, belonging to types of a character similar to those of the phospho-molybdates and phospho tungstates already described. I shall now show that such compounds may readily be formed by processes identical in principle with those which yield compounds of phosphoric and arsenic oxides with molybdic teroxide.

Vanadio-molybdates are formed when vanadic pentoxide V_2O_5 is digested with solutions of alkaline molybdates, more especially with the acid salts of potassium, sodium, or ammonium. The solution quickly becomes yellow, then, on heating, orange, and finally passes in many cases to deep orange-red. The vanadic oxide or acid employed must be perfectly free from vanadic dioxide, as this is also readily dissolved. The resulting compound then belongs to the class of triple complex acids, and contains both oxides of vanadium united to molybdic oxide. I shall return to these compounds in due time, and meanwhile shall refer to them under the name of vanadico-vanadio-molybdates. The presence even of a small quantity of vanadic dioxide may usually be detected by a peculiar greenish shade of color, easily recognised when once seen. This tint disappears when the solution is heated for a short time with bromine water or nitric acid, which readily oxidise the lower oxides of vanadium.

Vanadio-molybdates are also formed when solutions of alkaline vanadates and molybdates are heated together, and more readily when an excess of acid is present. The mixed solution then assumes at once a deep orange-red color.

The same salts are also formed when molybdic oxide, MoO_3, is boiled with a solution of an alkaline vanadate or meta-vanadate. Ammonic meta-vanadate, VO_3NH_4, may now be had in commerce in a state of very considerable purity, and has served as the starting point for much of my work. A solution of this salt readily dissolves molybdic oxide, forming one or more vanadio-molybdates, only in this case there is a tendency to a kind of supersaturation, a large excess of molybdic oxide being dissolved and separating from the liquid on cooling.

Finally, vanadio-molybdates may be formed by the decomposition of phospho-vanadio-molybdates, a class of triple compounds also to be described.

The vanadio-molybdates of the alkaline metals are in general readily soluble in water. They are highly crystalline, have a yellow or greenish-yellow, sometimes orange-yellow or orange-red color, and give in many cases crystalline precipitates with salts of the alkaline earths, of silver, and of thallium. They are not decomposed by boiling with excess of acid, and are usually very stable, except in the presence of reducing agents.

Analytical Methods.—The quantitative separation of molybdenum from vanadium presented a new problem in analytical chemistry, the solution of which cost much time and labor. It may be effected in two different ways. When the vanadium is wholly or partially in the form of vanadic dioxide, VO_2, it is to be oxidised by heating the concentrated solution with nitric acid. An alkaline carbonate is then to be added until the solution is nearly neutral, when the vanadic and molybdic oxides may be precipitated together by means of mercurous nitrate and mercuric oxide, precisely as in the estimation of tungstic oxide already described. The precipitate of mercurous vanadate and molybdate and mercuric oxide is to be filtered upon a paper filter. After drying, the filter and contents may be heated together in a platinum crucible, with free access of air. When the process is carefully conducted, the filter may be completely incinerated with great ease, and without loss of molybdic oxide from volatilisation. A weighed quantity of fused and pulverised neutral sodic tungstate is then to be added, when the crucible may be heated to redness, and the mercurous and mercuric oxides completely expelled. A second heating and weighing are always advisable. In this manner the sum of the weights of molybdic and vanadic oxides is obtained. To determine the quantity of vanadic oxide alone, the same process is to be repeated; only after burning off the filter the mass is to be carefully heated with a free supply of air to act mechanically until the whole of the molybdic oxide is volatilised and vanadic oxide remains as an orange-brown liquid, and, after cooling, as a crystalline mass. The complete expulsion of the molybdic oxide requires long heating, at a full red heat. The vanadic oxide is not volatile, but it has the inconvenient habit of creeping up the sides and over the edge of the crucible—a habit for which there appears to be no remedy. The weight of the molybdic oxide may then be determined by difference. This method gives good results, and in some cases may be used with advantage.

Another method is the following, which applies directly to the vanadio-molybdates of the alkaline metals, and to those of the alkaline earths, after the separation of the base. Ammonia is to be added in excess to the solution, which is then to be boiled for a few minutes, so as to convert the salt into a mixture of an alkaline vanadate and molybdate. A saturated solution of ammonic chloride is then added in very large excess, after which the liquid must be concentrated by continued boiling until reduced to a relatively small volume. The solution must then be allowed to stand for twenty-four hours, when a greater or less deposit of ammonic metavanadate will have formed in colorless crystals.[1] These crystals are to be brought upon an asbestos filter, and washed with a cold saturated and pure solution of ammonic chloride. The vanadic pentoxide may then be found by carefully igniting the salt with free access of air. It is, however, better to dissolve the salt upon the filter with boiling water, reduce the solution by means of a current of sulphydric acid gas after adding a little sulphuric acid, filter, and titrate with potassic hypermanganate. The clear blue solution contains vanadic dioxide only. The end reaction is tolerably sharp in dilute solutions—say 0.25 gram—of VO_2 in 250 cc. of water. The reason for adopting the method of titration is, that the ignition of ammonic meta-vanadate, even when conducted with great care, usually yields a mixture of vanadic pentoxide and dioxide, which it is difficult to oxidise completely. The precipitation of ammonic meta-vanadate by ammonic chloride is, as is well known, not absolutely complete, but the results of the analyses are on the whole fairly good.

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[1] The best commercial chloride of ammonium always contains iron not precipitable by ammonia. If bromine water be added first to the boiling solution, ammonia in small quantity separates the iron completely.

It is sometimes more advisable to employ a combination of the two methods described. After precipitating the two oxides by means of mercurous nitrate and mercuric oxide, the greater part of the molybdic oxide may be expelled by heat, after which the mixture of oxides, which now consists chiefly of vanadic pentoxide, may be dissolved in ammonia and treated with ammonic chloride in the manner above described. The quantity of molybdic oxide is most easily estimated by difference, the sum of the weights of the two oxides being determined by the method given above. It is not possible to reduce the vanadic pentoxide in the vanadio-molybdates to vanadic dioxide by means of sulphydric acid gas, by sulphurous oxide, or by any other reagent which I have tried, without at the same time reducing a portion of the molybdic teroxide to the blue oxide Mo_2O_5. This difficulty may, however, be overcome by first adding phosphoric acid to the solution in quantity about equal to the weight of the salt analysed. After the addition of a little sulphuric acid the reduction of the vanadic pentoxide may be effected either by boiling with a solution of sulphurous oxide, or by passing sulphydric acid gas for some time through the hot solution of the salt.

In separating vanadic from molybdic oxide by means of ammonic chloride it is necessary to keep the solution always slightly alkaline by the occasional addition of a little ammonia, since, as soon as the liquid becomes acid by the dissociation of the ammonium salts present, a vanadio-molybdate is again formed in greater or less quantity. To resolve a vanadio-molybdate into a mixture of vanadate and molybdate, it is necessary to employ an excess of free ammonia, and also to heat the solution. Actual boiling is most advantageous.

Another method of estimating vanadic oxide in the presence of molybdic teroxide consists in boiling the compound with strong chlorhydric acid, passing the chlorine set free into a solution of potassic iodide, and then determining the free iodine volumetrically by sodic hyposulphite and starch. I have not actually employed this method, however, though it gives excellent results in the analysis of the vanadio-tungstates.

It will be convenient to speak in this place of the best method of determining vanadium in alkaline vanadates without special reference to its separation from other elements. I find that this estimation may be effected with great accuracy by first oxidising any lower oxide which may be present by means of nitric acid to vanadic pentoxide, and then precipitating the faintly acid solution by mercurous nitrate and an excess of mercuric oxide at a boiling heat. Precipitation by mercurous nitrate alone was long since suggested by Berzelius, but the addition of mercuric oxide to render and to keep the solution neutral makes precisely the difference between a very accurate and an only tolerably good result. The precipitate may be collected upon a paper filter, and after washing with hot water ignited with free access of air. On cooling, a fine orange-brown crystalline mass of vanadic pentoxide remains. The filtrate from the precipitated oxides contains no appreciable trace of vanadium. The great facility with which a solution of vanadic pentoxide containing free chlorhydric acid is reduced by ferrous salts, suggested the possibility of determining vanadium by titration with ferrous sulphate, a solution of potassic ferricyanide being employed to determine the point of complete reduction.

A special study of this process was made in my laboratory by my assistant, Mr. Charles A. French, to whom the following details are exclusively due. The solution containing vanadic pentoxide is to be concentrated, and chlorhydric acid solution containing about one-tenth of its weight of pure acid added in large excess. After nearly saturating with a solution of ferrous or ammonio-ferrous sulphate of known titre, the solution is to be heated nearly to boiling, and the titration then completed with the ferrous salt, the end reaction being determined by trial drops upon a porcelain plate with a very dilute solution of potassic ferricyanide. Of this solution two drops of the ordinary laboratory reagent in a test-tube full of water give an appropriate strength. The process may be varied by adding the ferrous solution in excess, then titrating back by means of potassic dichromate of known titre, and finally adding the ferrous salt until the end reaction with ferricyanide is obtained. The ferrous solution may contain with advantage 0.005 gram of iron in one cubic centimeter. A sample of potassic divanadate containing no other impurity than a little potassic nitrate gave, by the gravimetric process above described, 65.12 per cent. V_2O_5. In three successive titrations with ammonio-ferrous sulphate Mr. French found 65.16, 65.27, and 64.95 per cent.

As ammonic meta-vanadate is now largely used in the manufacture of aniline black, and has become an article of commerce, the method of titration described above may perhaps find useful application in technical laboratories, as the end reaction in titrating with hypermanganate is not very sharp. I have in my work employed it in several cases as a check upon other methods.

In the analyses of vanadio-molybdates it is best to determine the alkalies by difference, as in the cases of the phospho-molybdates and phospho-tungstates. As in these cases also ammonia and water are best determined together by ignition with a weighed portion of neutral sodic tungstate, WO_4Na_2, a method suggested by Dr. F. A. Gooch for the whole class of phospho-tungstates and phospho-molybdates of ammonium; only in the case of the vanadio-molybdates and other salts containing both molybdenum and vanadium, it is necessary to be especially careful in igniting with the tungstate, because molybdic teroxide is sometimes given off before the complete fusion of the tungstate with the salt.

6 : 1 *Series.*—A solution of ammonic meta-vanadate, VO_3NH_4, readily dissolves molybdic teroxide on boiling, forming a deep orange-yellow solution. The liquid on standing deposits a very beautiful lemon-yellow salt, in sharp octahedral crystals, which are soluble in a rather large excess of cold water without sensible decomposition. The solution, on spontaneous evaporation, yields the salt without change. Of this salt—

1.1349 gram lost on ignition with WO_4Na_2 0.1806 gram = 15.91 per cent.

1.3220 gram lost on ignition with WO_4Na_2 0.2128 gram = 16.09 per cent.

1.5022 gram lost on ignition with WO_4Na_2 0.2412 gram $=$ 16.05 per cent.

1.2477 gram gave 0.2201 gram $NH_4Cl = 8.57$ per cent. $(NH_4)_2O$.

1.3822 gram gave 0.2439 gram $NH_4Cl = 8.57$ per cent. $(NH_4)_2O$.

1.2847 gram gave 0.1893 gram V_2O_5 by $KMnO_4 = 14.73$ per cent.

The analyses lead to the formula

$$6MoO_3.V_2O_5.2(NH_4)_2O + 5Aq,$$

which requires:

		Calc'd.	Found.		
$6MoO_3$	864	69.62			
V_2O_5	183	14.74	14.73		
$2(NH_4)_2O$	104	8.39	8.57	8.57	
$5H_2O$	90	7.25	7.34	7.52	7.48
	1241	100.00			

The reactions of a solution of this salt in cold water are as follows: No precipitate with salts of copper, zinc, manganese, and cadmium. Argentic nitrate gives a flocky yellow precipitate, with a tinge of buff. Mercurous nitrate gives a bright yellow precipitate. Thallous nitrate gives a very pale yellow flocky precipitate, which does not become crystalline on standing. Baric chloride gives no precipitate at first, but after a short time very beautiful sharp octahedral crystals; after longer standing, small pale yellow very distinct prismatic crystals also appear in the solution. Strontic chloride gives, after some days, very well defined pale yellow prismatic crystals. The solution of the vanadiomolybdate gives a rather dull yellow flocky precipitate with hydrochloride of brucin, and a bright yellow one with hydrochloride of strychnin. No precipitate is formed at first with potassic bromide, but after some days beautiful very well-defined granular crystals are deposited in quantity.

The solution of the salt has a strongly acid reaction. The mercurous salt is decomposed by dilute chlorhydric acid, with formation of mercurous chloride and a yellow acid solution, doubtless of the acid of this series. The acid was decomposed by spontaneous evaporation, and did not yield crystals.

It appears unnecessary to give a structural formula for the salt described, since we may regard V_2O_5 as simply replacing P_2O_5, and with the same function as this last, so that the structural formulas already given for the phosphotungstates will apply to the present case also.

Eight Atom Series.—When acid ammonic molybdate is dissolved, and vanadic pentoxide is added in small quantities at a time, the boiling solution quickly becomes yellow, and then orange. If the vanadic oxide is not perfectly free from dioxide, VO_2, a little bromine water should be employed to complete the oxidation. If a solution of baric chloride be mixed with the rather dilute and warm solution, no precipitate is formed at first, but after a few seconds an abundance of beautiful yellow well-defined crystals appears. These crystals are very sharp octahedra, and strongly resemble those of one of the ammonium salts of the six-molecule series. After a time granular yellow crystals make their appearance also in large quantity. The habitus of these crystals is so different from that of the first named that the two can readily be separated when mixed. A very approximate separation can also be effected by pouring off the liquid the moment that the granular crystals begin to appear. The yellow octahedral crystals are soluble in hot water, containing a little chlorhydric acid, and may be recrystallised. When heated, the salt swells up very much, and turns black, looking like coke. Of this salt—

1.0070 gram lost on ignition with WO_4Na_2 0.1310 gram = 13.00 per cent.

0.9716 gram lost on ignition with WO_4Na_2 0.1280 gram = 13.17 per cent.

1.2449 gram lost on ignition with WO_4Na_2 0.1637 gram = 13.16 per cent.

0.9682 gram gave 0.6534 gram $MoO_3 + V_2O_5$ = 67.48 per cent.
1.0162 gram gave 0.3029 gram SO_4Ba = 19.56 per cent.
1.0343 gram gave 0.3072 gram SO_4Ba = 19.50 per cent.
1.0190 gram gave 0.3023 gram SO_4Ba = 19.48 per cent.
1.0937 gram gave 0.0998 gram V_2O_5 = 9.12 per cent.
1.4395 gram gave 0.1356 gram V_2O_5 = 9.37 per cent.

These analyses lead to the formula

$$16MoO_3.2V_2O_5.5BaO + 29Aq,$$

or,

$$8MoO_3.V_2O_5.3BaO + 8MoO_3.V_2O_5.2BaO.H_2O + 28Aq,$$

which requires:

		Calculated.		Found.	
$16MoO_3$	2304	58.25		58.34	
$2V_2O_5$	364	9.21		9.12	9.37
$5BaO$	765	19.35	19.48		19.56
$29H_2O$	522	13.19	12.96	13.00	13.16
	3955	100.00			

The salt is therefore to be regarded as the acid salt of the eight-atom series, and belongs to a type of which several examples have been given among the phospho-tungstates and phospho-molybdates. It may also be considered as an acid sixteen-atom salt, upon the view which I have suggested in another place as at least possibly correct. The 16 : 2 barium salt is also formed when baric chloride is added to a solution of the 6 : 1 vanadio-molybdate of ammonium already described. The last-named salt is therefore formed when vanadic pentoxide is dissolved in acid ammonic molybdate, as well as when molybdic oxide is dissolved in ammonic meta-vanadate. In the double decomposition with baric chloride at least three molecules of the 6 : 1 ammonium salt must take part. The barium salt is nearly insoluble in cold water, but is soluble in much hot water, with partial decomposition and deposition of baric molybdate. The solution in cold water reddens litmus strongly; it gives with argentic nitrate a pale, and with mercurous nitrate a bright yellow flocky precipitate.

The first determination of vanadic pentoxide in this salt was made by heat alone, the mixture of molybdic and vanadic oxides being ignited until a constant weight was obtained. In the second analysis the determination was made by titration with ferrous sulphate after adding chlorhydric acid to the solution.

Eighteen Atom Series.—A boiling solution of ammonic meta-vanadate readily dissolves molybdic teroxide, MoO_3, forming a deep yellow or orange yellow solution. When the oxide is added as long as it is readily dissolved, an olive-green liquid is obtained, from which after twenty-four hours hard tabular crystals of a pale greenish color are deposited. These crystals are decomposed by boiling water, beautiful yellow needles very slightly soluble in water being formed, together with a greenish yellow solution which soon becomes turbid. The salt could not be purified by recrystallisation, and was therefore washed with a little cold water and dried on woollen paper. Of this salt—

0.8067 gram ignited with WO_4Na_2 lost 0.1586 gram $=$ 19.66 per cent.

0.8538 gram gave 0.2140 gram $NH_4Cl = 12.18$ per cent. $(NH_4)_2O$.

1.0243 gram gave 0.2526 gram $NH_4Cl = 11.99$ per cent. $(NH_3)_2O$.

0.7945 gram gave 0.0407 gram $V_2O_5 = 5.12$ per cent.

These analyses correspond to the formula

$$18MoO_3.V_2O_5.8(NH_4)_2O + 15Aq.$$

		Calculated.	Found.	
$18MoO_3$	2592	74.89	75.22	
V_2O_5	183	5.29	5.12	
$8(NH_4)_2O$	416	12.02	11.99	12.18
$15H_2O$	270	7.80	7.58	
	3461	100.00		

A more extended investigation will, undoubtedly, show that the vanadio-molybdates are, to say the least, numerous. The salts which I have described are sufficient to establish a parallelism between them and the phospho-molybdates, which is the more interesting because the chemical relations of vanadium are nearer to antimony than to phosphorus and arsenic. I shall return to this point, however, in describing and discussing the class of antimonio-tungstates and antimonio-molybdates.

VANADIO-TUNGSTATES.

Vanadio-tungstates are very readily formed under conditions precisely the same as those which determine the formation of vanadio-molybdates, and which it is unnecessary to recapitulate. As a class they have a yellow, orange, or orange-red color. They are, so far as examined, readily soluble in water, are crystalline and extremely stable in composition, in the sense at least that it is often difficult to separate the combined vanadic and tungstic oxides, though in many cases complex salts easily break up into compounds of simpler type.

Analytical Methods.—When alkaline vanadates and tungstates are simply mixed together under conditions which do not result in the formation of vanadio-tungstates, it is possible to effect the separation of the vanadic and tungstic oxides by means of a solution of ammonic chloride, which, as is well known, precipitates ammonic meta-vanadate in colorless crystals nearly insoluble in a saturated solution of ammonic chloride. This method cannot be applied directly to the separation of the two oxides when combined, as in the vanadio-tungstates, but the difficulty can be overcome by either of the following methods. An excess of ammonia is to be added to the solution, which is then to be digested, or, if necessary, boiled until the liquid becomes colorless. By this process, which, however, does not always perfectly succeed, the vanadio-tungstate is resolved into a mixture of ammonic tungstate and meta-vanadate. In place of ammonia, sodic or potassic hydrate in excess may be employed, and frequently with advantage. After the resolution of the vanadio-tungstate, as indicated by the color of the liquid, ammonic meta-vanadate may be precipitated by boiling with an excess of ammonic chloride. From the cold solution completely saturated with ammonic chloride the meta-vanadate may be separated by filtration, and the vanadic pentoxide estimated in the manner already pointed out. A variation of this process, which may often be employed with advantage, consists in fusing the vanadio-tungstate with an excess of potassic or sodic carbonate in a platinum crucible. The fused mass must be boiled with a strong solution of ammonic chloride, a drop or two of ammonia being added from time to time to keep the solution distinctly alkaline. The ammonic meta-vanadate is to be separated and treated as above. In applying these methods it is important in each case to be sure that the vanadium is exclusively in the form of pentoxide. It is therefore always advisable to add a little bromine water to the solution of the vanadio-tungstate before adding the excess of ammonia. In fusing with alkaline carbonates a little potassic or sodic nitrate may be added to the mixture in the crucible. In this manner we may avoid the error which would result from the presence of vanadic dioxide in the small quantity which often exists in consequence of the reducing agency of dust or traces of organic matter.

After a great number of trials, the methods given above are the only ones by which I have found it possible to effect even an approximate separation of vanadic and tungstic oxides in combination.

In place of the actual separation of the oxides, it is much more convenient, and I believe also in general much more accurate, to employ the following process, which permits us to estimate vanadium quantitatively in presence of tungstic, as well as of various other oxides. This process depends upon the fact that vanadic pentoxide, either free or in combination, when boiled with strong chlorhydric acid, evolves chlorine, which may be collected in a solution of potassic iodide. The iodine set free may then be estimated with great accuracy by means of sodic hyposulphite after adding a solution of starch.

The fact that vanadic pentoxide evolves chlorine on heating with chlorhydric acid was, so far as I have been able to find, first remarked by Mohr, who in his well-known work on volumetric analysis suggested as possible the method of determining vanadium which I have employed, without, however, testing it in any single case.

It is possible, in some cases at least, to determine vanadic pentoxide in the presence of tungstic oxide by titration with hypermanganate. To the solution of the substance containing both metals, phosphoric and sulphuric acids are to be added, and the vanadic pentoxide is then to be reduced to dioxide by means of sulphydric acid gas passed into the boiling solution until complete reduction is obtained. No appreciable quantity of tungstic oxide is reduced under these circumstances. The titration with hypermanganate may then usually, though not always, be executed, and gives a fairly good result.

Finally, the method of titration by ferrous salts may often be used with success. The details have already been given, and do not need to be repeated.

5:1 *Vanadio-tungstate of Ammonium.*—When 12:5 ammonic tungstate is boiled with a solution of ammonic meta-vanadate an orange solution is obtained, which on evaporation deposits orange-yellow crusts of indistinct crystals. The color of this salt is somewhat dull; it is not very soluble in cold, but soluble in boiling water, and may be recrystallised without sensible decomposition. The salt becomes greenish upon the surface when dried upon woollen paper, from a slight superficial reduction of the vanadic pentoxide. Of this salt—

1.0558 gram gave 0.1222 gram $(NH_4)_2O$ by titration = 11.57 per cent.

1.1873 gram lost on ignition 0.2922 gram = 24.61 per cent. H_2O and NH_3.

1.0558 gram gave by titration with $KMnO_4$ 11.09 per cent. V_2O_5.

The analyses lead to the formula

$$5WO_3.V_2O_5.4(NH_4)_2O + 13Aq,$$

or

$$5WO_3.V_2O_5.4(NH_4)_2O.2H_2O + 11Aq,$$

if we regard the acid provisionally as 6-basic, which requires :

		Calculated.	Found.
$5WO_3$	1160	64.99	...
V_2O_5	183	10.26	11.09
$4(NH_4)_2O$	208	11.65	11.57
$13H_2O$	234	13.10	13.04
	1785	100.00	

The percentage of vanadic oxide found is too high, but there can be no reasonable doubt as to the formula. I obtained the salt but once, and then in small quantity. The solution gives a dull yellow flocky precipitate with argentic and mercurous nitrates, and after a time a yellow crystalline precipitate with excess of potassic bromide. The ammonium salt is interesting as being probably the first term in a series. It corresponds to the phospho-molybdate

$$5MoO_3.P_2O_5.3(NH_4)_2O.3H_2O + 4Aq.$$

The following may serve as starting points for further investigation. When normal baric tungstate, WO_4Ba, is boiled for a long time with a solution of ammonic meta-vanadate, it is very slowly dissolved to an orange-yellow solution, which on cooling gives very beautiful square tabular deep red crystals mixed with excess of baric tungstate. 12 : 5 baric tungstate dissolves more readily in the meta-vanadate, and gives a bright orange-yellow solution, which on evaporation yields fine prismatic crystals. From the above it appears probable that the tungstates of the heavy metals, both neutral and acid, will yield vanadio-tungstates by boiling with alkaline vanadates, and possibly in this manner various new series of salts may be formed. The costliness of the material for this work has prevented a more thorough study on my own part.

10 : 1 *Vanadio-tungstic Acid.*—A solution of ammonic meta-vanadate dissolves tungstic oxide readily on boiling, giving a deep orange-yellow solution. After long boiling with an excess of the oxide, the clear deep orange filtrate gives, with a solution of chloride of trimethylammonium, on standing some hours, two distinct

kinds of crystals, which are respectively yellow and deep orange-red. There are therefore, apparently at least, two different salts formed in the solution of the tungstic oxide. The solution of the ammonium salt gave with baric chloride, after some hours, sharp octahedral crystals of a yellow salt, but slightly soluble even in hot water. In a second experiment, baric chloride gave at once a yellow fine-grained crystalline insoluble precipitate; but the precipitation was not complete. On boiling the mixture of oxides obtained by igniting ammonic meta-vanadate in air with 12 : 5 sodic tungstate, I obtained a greenish-orange solution. This was oxidised by boiling with nitric acid, when it became orange. On standing, the acid solution deposited a relatively large quantity of a sulphur-yellow crystalline body, which was but very slightly soluble in cold water, and required a large quantity of hot water for complete solution. This substance was drained upon the filter-pump, washed with cold water, and dried upon woollen paper. Of this preparation—

0.8331 gram lost on ignition 0.1188 gram = 13.42 per cent.
0.8331 gram gave 0.7192 gram $WO_3 + V_2O_5$ = 86.03 per cent.
0.9786 gram gave 0.8411 gram " = 85.95 per cent.
1.0846 gram gave 0.0718 gram V_2O_5 = 6.62 per cent.

The analyses correspond with the formula

$$10WO_3.V_2O_5.6H_2O + 16Aq,$$

which requires:

		Calculated.		Found.	
$10WO_3$	2320	80.53	86.88	80.30	86.92
V_2O_5	183	6.35		6.62	
$22H_2O$	378	13.12		13.08	
	2899	100.00			

I did not succeed in obtaining salts corresponding to the 10 : 1 acid above described by saturating the acid with alkaline bases, as mixtures of the acid with alkaline vanadates and tungstates were formed until the point of complete saturation was reached.

18 : 1 *Vanadio-tungstic Acid.*—The orange-yellow mother liquor from which the 12 : 1 acid separated gave on evaporation beautiful crystalline needles of a second acid, the formula of which is

$$18WO_3.V_2O_5.6H_2O + 30Aq.$$

Of this acid,

1.0343 gram lost on ignition 0.1342 gram = 12.97 per çent. water.
1.0343 gram gave 0.0363 gram V_2O_5 = 3.51 per cent.

1.2540 gram lost on ignition 0.1617 gram = 12.90 per cent. The formula requires:

		Calculated.		Found.		
$18WO_3$	4176	83.40	87.05		83.55	87.06
V_2O_5	183	3.65			3.51	
$36H_2O$	648	12.95		12.90	12.97	
	5007					

The sum of the two oxides is determined by difference, which is the most accurate method whenever applicable. In this, as in all the other vanadio-tungstic compounds analysed, the vanadic pentoxide was determined by boiling with chlorhydric acid in the manner already described. The crystals of the 18 : 1 acid are readily soluble in water, and may be recrystallised without decomposition.

The compounds which I have described appear to establish a complete analogy between the vanadio-tungstates and phospho-tungstates already described. Rammelsberg[1] has described a salt which crystallises in beautiful brown-black cubo-octahedrons, and which he obtained by saturating a commercial sodic vanadate with acetic acid and evaporating spontaneously. According to his analyses, the salt has the formula

$$(NH_4)_2O.WO_3.3V_2O_5 + 6Aq.$$

I suspect that it contains VO_2 as well as V_2O_5. I did not succeed in preparing it by synthesis, employing pure VO_3NH_4 and $WO_4(NH_4)_2$. It may prove to be the type of an entirely new class of complex acids, and well deserves further investigation.

(To be continued.)

Contributions from the Chemical Laboratory of Harvard College.

XXXVI.—β-PHENYLTRIBROMPROPIONIC ACID.[2]

By Leonard P. Kinnicutt and George M. Palmer.

α-Phenyltribrompropionic acid and the products formed when this acid is decomposed by boiling water were briefly described by one of us last year.[1] During the past winter the study of the β acid was undertaken, and it has been considered best to give at this time the results so far obtained, as the further investigation must be carried on in different relations.

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[1] Berichte der deutschen chemischen Gesellschaft, 1, 161.

[2] Communicated by the Authors, from the Proceedings of the American Academy of Arts and Sciences.

β-Phenyltribrompropionic acid was obtained by the action of dry bromine on β-monobromcinnamic acid, this last having been prepared in the way previously described.[2]

By the action of bromine on β-monobromcinnamic acid, Glaser[3] obtained an acid, which he describes as melting during the absorption of the bromine and only solidifying again after several days. The melting point he found to be 45–48° C. The results obtained by us are very different. Perfectly pure β-monobromcinnamic acid melting at 120° C. was placed under a bell glass with the theoretical amount of bromine. Not the slightest indication of melting was observed, and after twenty-four hours the bromine was all absorbed. The acid so obtained was purified by crystallisation from chloroform and melted at 151° C. It is soluble in alcohol, ether, carbonic disulphide, chloroform, and benzol.

The analyses gave the following results:

1. 0.2711 gram substance gave 0.2788 gram CO_2 and 0.0454 gram H_2O.

2. 0.3845 gram substance gave 0.3912 gram CO_2 and 0.0702 gram H_2O.

3. 0.1894 gram substance gave 0.2769 gram AgBr.

4. 0.1839 gram substance gave 0.2696 gram AgBr.

Calculated for $C_9H_7Br_3O_2$.		Found.			
		1.	2.	3.	4.
C	27.9	28.04	27.73	...	...
H	1.8	1.86	2.00	...	...
Br	62.17	...	...	62.24	62.40

Decomposition of β-Phenyltribrompropionic Acid by Water heated to 100° C.

Twenty grams of the acid were placed in a flask with two hundred cubic centimeters of boiling water. Decomposition began immediately, a volatile oil separating out, which at the end of eight hours had for the greater part been carried over with the steam, leaving a clear liquid that on cooling deposited a white crystalline substance. On examination, the oil was found to be a dibromstyrol, the white crystalline substance the α-monobromcinnamic

[1] Kinnicutt, this Journal, **3**, 4.

[2] *Ibid.*

[3] Annalen der Chemie, **143**, 339.

acid, and a third substance, which remained in solution in the liquid, gave on analysis results corresponding very closely to those required for a phenyldibromlactic acid.

Dibromstyrol, $C_8H_6Br_2$.

The oil that was carried over by the steam was separated from the water by ether, and, after thorough washing to remove all traces of hydrobromic acid, the ether was distilled off. The oil thus obtained was of a light amber color, growing gradually darker, and giving off on long standing traces of hydrobromic acid.

It boils at 253–254° C. with slight decomposition, hydrobromic acid being formed.

The analyses of the oil, dried over sulphuric acid, gave the following results:

1. 0.2518 gram substance gave 0.3328 gram CO_2 and 0.0518 gram H_2O.

2. 0.3592 gram substance gave 0.4810 gram CO_2 and 0.0744 gram H_2O.

3. 0.2518 gram substance gave 0.3615 gram AgBr.

4. 0.3032 gram substance gave 0.4379 gram AgBr.

Calculated for $C_8H_6Br_2$.		Found.			
		1.	2.	3.	4.
C	36.64	36.02	36.50	...	...
H	2.29	2.26	3.20	...	...
Br	61.06	...	...	61.10	61.40

The properties of this oil correspond in all respects with those of the dibromstyrol obtained from the decomposition of the α-phenyltribrompropionic acid,[1] and it seems most probable that the two substances are not simply isomeric, but identical. This point, however, cannot be positively settled till a careful study has been made of the addition products of both compounds.

α-Monobromcinnamic Acid.

The nearly clear liquid from which the bromstyrol had been distilled was made slightly alkaline with sodic carbonate, and shaken with ether to remove the last traces of the oil. The solution was then evaporated to a volume of about one hundred cubic centimeters and acidified with dilute hydrochloric acid. A white precipitate was thrown down, which after one crystallisation from boiling water melted at 132° C., and proved to be the α-monobromcinnamic acid.

[1] Kinnicutt, this Journal, **3**, 4.

Two bromine determinations gave the following results:

1. 0.1986 gram substance gave 0.1661 gram AgBr.
2. 0.2242 gram substance gave 0.1874 gram AgBr.

	Calculated for $C_9H_7BrO_2$.	Found. 1.	Found. 2.
Br	35.25	35.58	35.56

The barium salt, formed by adding baric chloride to a dilute solution of the acid in warm water, resembled in every respect the barium salt of α-monobromcinnamic acid as described by Glaser.[1] It was only slightly soluble in cold water and insoluble in alcohol. The barium salt of the β-bromcinnamic acid is hygroscopic, and soluble in alcohol.

The salt gave on analysis the following result:

0.3092 gram substance gave 0.1233 gram $BaSO_4$.

	Calculated for $(C_9H_6BrO_2)_2Ba$.	Found.
Ba	23.23	23.42

The formation of the α-monobromcinnamic acid from both the α- and β-phenyltribrompropionic acids was rather to be expected, as Glaser has found that the β-monobromcinnamic acid is changed into the α by distillation, or by heating it with hydriodic acid,[2] and, moreover, Barish has shown that from both the α and β acids only the ethyl ether of the α acid can be obtained.[3]

Phenyldibromlactic Acid.

On evaporating the filtrate from the α-monobromcinnamic acid to a small volume, a substance crystallised out that melted at about 180° C. After recrystallisation several times from water, the melting point rose to 184° C., and it gave on analysis amounts of carbon, hydrogen, and bromine corresponding to those required for a phenyldibromlactic acid.

The acid is very soluble in water, alcohol and ether, soluble in chloroform, and slightly soluble in carbonic disulphide and benzol.

We have not as yet succeeded in obtaining the acid in large enough quantities to study its salts, or to decide which of the several possible formulae correctly represents its structure.

The analyses gave the following results:

1. 0.1854 gram substance gave 0.2257 gram CO_2 and 0.0440 gram H_2O.

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[1] Annalen der Chemie, **143**, 334.

[2] *Ibid.* 336.

[3] Jour. für prakt. Chemie, **128**, 185.

2. 0.1989 gram substance gave 0.2440 gram CO_2 and 0.0470 gram H_2O.

3. 0.1605 gram substance gave 0.1870 gram AgBr.

4. 0.1812 gram substance gave 0.2122 gram AgBr.

Calculated for $C_9H_8Br_2O_3$.		Found.			
		1.	2.	3.	4.
C	33.34	33.21	33.42	...	...
H	2.46	2.63	2.62	...	...
Br	49.37	...	...	49.60	49.70

Action of Bromine on Dibromstyrol.

The dibromstyrol obtained from the decomposition of the β-phenyltribrompropionic acid was placed under a bell glass, with an excess of bromine. The oil gradually thickened, and after two days had absorbed about its own weight of bromine. It was then placed over quicklime, and after remaining there three or four days was washed thoroughly with water, and then separated from the water by shaking with ether. The so purified oil gave on analyses the following amounts of bromine:

1. 0.2050 gram substance gave 0.3646 gram AgBr.
2. 0.2110 gram substance gave 0.3737 gram AgBr.
3. 0.2055 gram substance gave 0.3651 gram AgBr.

Calculated for $C_8H_6Br_4$.		Found.		
		1.	2.	3.
Br	75.82	75.68	75.34	75.60

The substance is evidently a tetrabromstyrol. It is a thick viscous oil, soluble in alcohol, ether, and carbonic disulphide. It begins to decompose on heating at a comparatively low temperature.

It is to be hoped that the study of the products formed by the action of boiling water or dilute alkalies on the above compound, and also on the substance obtained by the addition of bromine to the dibromstyrol formed from α-phenyltribrompropionic acid, will not only show the structure of the two dibromstyrols, but will also give a more direct proof of the structure of the two monobromcinnamic acids than that obtained by Schotten.[1]

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[1] Berichte der deutschen chemischen Gesellschaft, **15**, 1947.

XXXVII.—THE VOLUMETRIC DETERMINATION OF COMBINED NITROUS ACID.

By Leonard P. Kinnicutt and John U. Nef.

The amount of nitrous acid contained in commercial samples of potassic and sodic nitrites has been commonly determined in the following manner. The nitrites are dissolved in slightly acidulated water; a solution of potassic permanganate is added till the oxidation of the nitrous acid is nearly completed; the solution is then made strongly acid, and potassic permanganate added until the solution has a faint red color.

This method is far from satisfactory, closely agreeing results being rather the exception than the rule. The cause is most probably due to the escape of a small amount of nitrous acid, and also to the slow oxidation of the last traces of the nitrous acid by the potassic permanganate.

A further study of the analyses of nitrites volumetrically seemed desirable, and after numerous experiments the following process, or modification of the old process, as it might more properly be called, was devised.

The sample of nitrite is dissolved in cold water, one part of the salt to at least three hundred parts of water. To this solution a deci-normal solution of potassic permanganate is added, drop by drop, till the liquid has a decided and permanent red color, then two or three drops of dilute sulphuric acid, and immediately afterwards an excess of the potassic permanganate solution. The liquid, which should now be of a dark red color, is made strongly acid with sulphuric acid, heated to boiling, and the excess of potassic permanganate determined by means of a deci-normal solution of oxalic acid.

Analyses of samples of both potassic and sodic nitrites, made in accordance with the above modification, show that results agreeing very closely with one another can easily be obtained.

Potassic Nitrite Solution.

[One litre contained 4.3550 grams.]

Taken.	KNO_2 found.
25 cc. = 0.1089 gram	0.09194 gram = 84.44 per cent.
35 cc. = 0.1525 “	0.1289 “ = 84.48 “
40 cc. = 0.1742 “	0.1472 “ = 84.51 “
55 cc. = 0.2395 “	0.2024 “ = 84.49 “
60 cc. = 0.2613 “	0.2210 “ = 84.53 “

Sodic Nitrite Solution.

[One litre contained 3.090 grams.]

Taken.	$NaNO_2$ found.
25 cc. = 0.0919 gram	0.07713 gram = 83.95 per cent.
35 cc. = 0.1287 "	0.1082 " = 84.07 "
45 cc. = 0.1654 "	0.1390 " = 84.05 "
53 cc. = 0.1949 "	0.1639 " = 84.03 "
60 cc. = 0.2206 "	0.1854 " = 84.05 "

The volumetric method for the determination of sulphites is also most unsatisfactory. The study of this subject was therefore given to Mr. R. Penrose, a student in this laboratory. He experimented both with potassic permanganate and oxalic acid as above, and also with iron alum and the permanganate; but, although many variations of these processes were tried, and the work carefully conducted, the results were not satisfactory.

Communications from the Chemical Laboratory of Rutgers College.

XII.—THE PURIFICATION OF AMMONIUM FLUORIDE.

By Peter T. Austen and Francis A. Wilber.

One of the most convenient methods of determining silica in titaniferous and other ores is to expel it as fluoride by means of ammonium fluoride and sulphuric acid, or by fluorhydric acid alone. But the practical difficulty here met is the impossibility of getting either ammonium fluoride or fluorhydric acid in a pure state, for it is of course absolutely necessary that they should leave no residue after volatilisation. The following procedure has enabled us to use the articles obtainable in commerce with excellent results.

The amount of ammonium fluoride necessary for the analysis is dissolved in as little water as possible in a platinum dish, and strong ammonia added in slight excess. If fluorhydric acid is used the ammonia is added in small amounts from a pipette, so as to avoid spitting. In this case the operation is of course performed under a good hood. In both cases a voluminous precipitate will be obtained. A five-inch filter paper, which has previously been extracted[1] with fluorhydric acid to remove silica, is folded to the sixteenth fold, making a cone of an angle of about 67°. If the papers are very thin it is well to take two of them and fold them together. This cone is then placed in a ring of stout platinum wire, which may be conveniently held in the ring of a ring-stand by three smaller platinum wires. The liquid is decanted into this filter and allowed to filter at once into the platinum crucible containing the ore. The crucible is then placed on a water-bath and the liquid concentrated. This step is not necessary unless the bulk of the liquid is large or the crucible small, and indeed had better be avoided, since ammonium fluoride is quite volatile. The liquid is next made acid with sulphuric acid, evaporated to dryness and ignited as usual. Should it be feared that the silica had not been entirely expelled, the operation should be repeated, but it will be found that as a rule one treatment is sufficient. The ammonium fluoride prepared in this way we find does not leave any appreciable residue. Of course every new lot of ammonium fluoride or fluorhydric acid, before being used in analysis, should be tested for residue after treatment in this manner.

We prefer to use the acid in analysis, purifying it and converting it into the ammonium salt by the above method, for its cost is but one-third of that of the ammonium fluoride and it affords a more concentrated solution.

NEW BRUNSWICK, N. J.

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[1] Papers freed from ash by treatment with chlorhydric and fluorhydric acids are now manufactured by Schleicher and Schüll by a method described by me in 1878 (Chemical News, **37**, 149) and tested and approved by Profs. Fresenius and Caspari (Zeitschrift für analytische Chemie, **22**, 241).—P. T. A.

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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

By Wolcott Gibbs, M. D.
Rumford Professor in Harvard University.

[Continued from p. 383.]

PHOSPHO-VANADIO-MOLYBDATES.

Triple acids of this class are formed when solutions of phospho-vanadates are digested with molybdic teroxide; when vanadio-molybdates and alkaline phosphates are heated together in solution, especially in the presence of an acid; and when vanadic pentoxide is heated with a solution of an alkaline phospho-molybdate.

The salts of this class are as a whole less stable than the vanadio-molybdates. They are, however, very well defined, and usually highly crystalline. In color they vary from an orange to a deep garnet, or ruby red. In general character they closely resemble the salts of the double compounds already described, and are often very beautiful.

Analytical Methods.—These are for the most part similar to those which I have already described. The three oxides may be precipitated together by mercurous nitrate and mercuric oxide, and then ignited with sodic tungstate in the manner described for the analysis of phospho-molybdates and arsenio-molybdates. The phosphoric oxide cannot be determined with accuracy by direct precipitation with magnesia-mixture. It is necessary first to remove the vanadic oxide. This may be done by dissolving the salt, adding ammonia in small but distinct excess, and afterward ammonic nitrate in large quantity. The solution is to be boiled for a short time, care being taken that after boiling free ammonia shall still be present. After standing in the cold for twenty-four hours the precipitated ammonic meta-vanadate may be filtered off, washed with a cold concentrated solution of ammonic nitrate, and titrated in the manner which I have described in speaking of the vanadio-molybdates. In the filtrate from the meta-vanadate phosphoric oxide may be determined by double precipitation with magnesia-mixture and final treatment with ammonic sulphide. Molybdic oxide is best determined by difference, the sum of the weights of the three oxides being known. Water, ammonia, and basic oxides may be found by the methods which I have already described in the cases of the binary compounds.

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[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

48:2:1 *Series.*—When 10:2 acid phospho-molybdate of ammonium, $10MoO_3.2P_2O_5.5(NH_4)_2O + 6Aq$, and ammonic meta-vanadate are dissolved together, there appears to be no reaction; but if a small excess of chlorhydric acid is added, and the solution is boiled, a beautiful deep orange-red crystalline precipitate is formed at once. This may be drained on a filter and washed with cold water, in which it is but slightly soluble. Hot water dissolves it rather more freely, but the salt cannot be purified by recrystallisation, as it is more or less completely decomposed by solution. Ammonia water dissolves it, forming a colorless liquid, in which baric acetate produces a nearly colorless precipitate. Of this salt,

1.3011 gram lost on ignition with WO_4Na_2 0.1399 gram = 10.75 per cent. $NH_3 + H_2O$.

1.0425 gram lost on ignition with WO_4Na_2 0.1124 gram = 10.78 per cent. $NH_3 + H_2O$.

1.5611 gram gave 0.1361 gram NH_4Cl = 4.24 per cent. $(NH_4)_2O$.

1.0113 gram gave 0.0900 gram NH_4Cl = 4.32 per cent. $(NH_4)_2O$.

1.3997 gram gave with MnO_4K 0.0304 gram V_2O_5 = 2.17 per cent.

$\left\{\begin{array}{l}\text{1.9173 gram gave with } MnO_4K \text{ 0.0463 gram } V_2O_5 = 2.41 \text{ per cent.}\\ \text{1.9173 gram gave 0.1112 gram } P_2O_7Mg_2 = 3.71 \text{ per cent. } P_2O_5.\end{array}\right.$

In the last two analyses the vanadic pentoxide was first separated by ammonic nitrate as VO_3NH_4; the phosphoric oxide was then determined in the filtrate.

The analyses correspond fairly well with the formula

$$48MoO_3.2P_2O_5.V_2O_5.7(NH_4)_2O + 30Aq.$$

		Calculated.	Mean.	Found.	
$48MoO_3$	6912	83.45	83.23	83.23(diff.)	
$2P_2O_5$	284	3.43	3.71	3.71	
V_2O_5	183	2.21	2.29	2.17	2.41
$7(NH_4)_2O$	364	4.39	4.28	4 32	4.24
$30H_2O$	540	6.52	6.50	6.50	6.51
	8283	100.00			

The compound may be regarded as a double salt, with the formula

$$2[16MoO_3.P_2O_5.2(NH_4)_2.H_2O] + 16MoO_3.V_2O_5.3(NH_4)_2O + 28Aq,$$

though, of course, other arrangements of the constituents are, in the present state of our knowledge, equally probable. Thus, we may also represent the results of the analyses by the expression,

$$2[12MoO_3.P_2O_5.2(NH_4)_2.H_2O] + 24MoO_3.V_2O_5.3(NH_4)_2O + 28Aq.$$

14 : 1 : 8 *Series.*—The beautiful yellow crystalline phospho-molybdates of ammonium, containing respectively twenty-four and twenty-two molecules of MoO_3 to one molecule of phosphoric oxide, slowly dissolve when boiled with a solution of ammonic meta-vanadate, giving a very fine deep orange-red liquid. After standing a few hours, the solution gives splendid deep ruby-red crystals in large quantity. These crystals appear to be octahedra; they dissolve readily in hot water to a deep orange-red liquid, without undergoing any apparent decomposition, and the salt crystallises from the solution unchanged. The solution gives no precipitate at first with baric chloride, but after a time very fine garnet-red crystals are formed in small quantity, mixed with a pale orange flocky or indistinctly crystalline substance, with an orange-red supernatant liquid. Potassic bromide in large excess gives an orange crystalline, and argentic nitrate a cinnamon-colored not distinctly crystalline precipitate. Mercurous nitrate and plumbic acetate gave orange precipitates. A solution of chloride of tri-

methyl-ammonium, $N(CH_3)_3HCl$, gives an orange precipitate in the concentrated solution, soluble in boiling water, and crystallising in beautiful small granular crystals, which are orange with an aurora-red tint. The crystals of the ruby-red salt became duller upon the surfaces when dried on woollen paper, but did not distinctly effloresce. Of this salt,

1.0686 gram lost on ignition with WO_4Na_2 0.2833 gram = 26.51 per cent. NH_3 and H_2O.

1.3051 gram gave 0.2245 gram NH_4Cl = 8.36 per cent. $(NH_4)_2O$.

1.1020 gram gave 0.3253 gram V_2O_5 = 29.51 per cent.

1.1113 gram gave 0.0598 gram $P_2O_7Mg_2$ = 3.44 per cent. P_2O_5.

The analyses lead to the formula,

$$14MoO_3.P_2O_5.8V_2O_5.8(NH_4)_2O + 50Aq.$$

		Calculated.		Found.	
$14MoO_3$	2016	40.83	73.36	40.54	73 49
$8V_2O_5$	1464	29.64		29.51	
P_2O_5	142	2.89		3.44	
$8(NH_4)_2O$	416	8.42		8.36	
$50H_2O$	900	18.22		18.14	
	4938	100.00			

If we assume that in this salt vanadic pentoxide stands in a relation to phosphoric oxide exactly analogous to that of molybdic teroxide, the compound will be of the same type as the phosphomolybdate already described,

$$22MoO_3.P_2O_5.xR_2O,$$

since we may write V_2O_5 as if its rational formula were $V_2O_2.O_3$.

In some preparations of this salt I observed the formation of two other salts in relatively small quantity. One of these formed pale orange-colored needles; the other, glimmering scales but slightly soluble in hot water.

PHOSPHO-VANADIO-TUNGSTATES.

These compounds bear a general resemblance to the phospho-vanadio-molybdates already described, and may be prepared by similar processes. They have usually a more or less deep orange or orange-red color, and very often exhibit a peculiar and highly characteristic aurora-red tint. They are crystalline and well defined, and many salts of the different series are very beautiful.

Analytical Methods.—In all these salts it will, as in similar cases, be found most advantageous to determine the three acid-forming oxides by means of mercurous nitrate and mercuric oxide in the manner already pointed out. The estimation of phosphoric oxide may usually be made with a fair approximation to precision by direct precipitation with magnesia-mixture in the ammoniacal solution, redissolving the ammonio-magnesic phosphate, and precipitating a second time. In some cases I have found it better first to reduce the vanadic pentoxide to vanadic dioxide by boiling with strong chlorhydric acid, evaporating to dryness, and redissolving with the addition of a little tartaric and chlorhydric acids. A perfectly satisfactory method of estimating phosphoric oxide in these compounds remains to be discovered. Vanadic pentoxide may be estimated with accuracy by the methods already pointed out for the analysis of the vanadio-tungstates; that is, by boiling with strong chlorhydric acid, collecting the chlorine evolved in a solution of potassic iodide, and determining the free iodine by titration with sodic hyposulphite. A solution of potassic hypermanganate does not always oxidise vanadic dioxide in presence of tungstic, phosphoric, and free sulphuric acid, or only with great difficulty, so that the method is not generally applicable for the analysis of this class of compounds. Nitric acid, however, readily oxidises the dioxide under the same circumstances.

60 : 3 : 1 *Series.*—When the white insoluble phospho-tungstates of ammonium containing twenty-two or twenty-four molecules of tungstic to one of phosphoric oxide are dissolved in ammonia water, and a solution of ammonic meta-vanadate is added, no precipitate is formed; but if a small excess of chlorhydric acid is present in the boiling liquid, a fine lemon-yellow crystalline precipitate soon forms, which is to be well washed with a cold dilute solution of ammonic nitrate, as otherwise the salt passes readily through the filter, giving a milky liquid. The final washing may be made with a very dilute solution of the nitrate. After drying on woollen paper, the salt closely resembles tungstic oxide in color. It is almost insoluble in cold, and but slightly soluble in hot water, but with a large excess of ammonic phosphate it dissolves to a yellow solution; with ammonia water it gives a colorless solution. In a solution of ammonic carbonate it dissolves with strong efferves-

cence, indicating its distinctly acid character. The salt is not readily reduced by boiling with sulphuric and sulphurous acids, or by citric acid in the presence of chlorhydric acid, but easily by boiling with a strong solution of potassic cyanide, and, as is usual with this class of compounds, by fusion with the same salt.

Of this compound,

2.0684 grams lost on ignition with WO_4Na_2 0.2068 gram = 10.00 per cent. NH_3 and H_2O.

1.0971 gram gave 0.0747 gram $NH_4Cl = 3.31$ per cent. $(NH_4)_2O$.

1.3424 gram gave 0.0568 gram $P_2O_7Mg = 2.71$ per cent. P_2O_5.

2.5488 grams gave 0.1102 gram $P_2O_7Mg = 2.77$ per cent. P_2O_5.

1.0555 gram gave 0.0123 gram $V_2O_5 = 1.16$ per cent.

The analyses correspond very closely to the formula,

$$60WO_3.3P_2O_5.V_2O_5.10(NH_4)_2O + 60Aq,$$

which requires:

		Calculated.		Found.		
$60WO_3$	13920	86.29	90.00	86.10 (diff.)		90.00
$3P_2O_5$	426	2.64		2.71	2.77	
V_2O_5	183	1.15		1.16		
$10(NH_4)_2O$	520	3.23	9.92	3.31		10.00
$60H_2O$	1080	6.69		6.69		
	16129	100.00				

The compound is very probably a double salt, and may have the formula,

$$3[16WO_3.P_2O_5.3(NH_4)_2O] + 12WO_3.V_2O_5.(NH_4)_2O.2H_2O + 58Aq.$$

The arrangement of the constituents is here, of course, purely arbitrary, and must be regarded as only provisional. In the analyses above given the phosphoric oxide was determined directly and by double precipitation. The vanadic oxide was determined by boiling with chlorhydric acid and titration, in the manner already described.

16 : 1 : 3 *Series.*—A boiling solution of ammonic meta-vanadate dissolves the white insoluble phospho-tungstates of ammonium quite readily to a very deep orange-red solution. After standing some days, large deep orange or garnet-red crystals separate in quantity. They appear to be octahedra, and when first separated from the mother liquor are very beautiful; but on standing in the air they

lose their lustre, perhaps from a superficial effervescence, and become dull red. The salt is readily soluble in water, giving a deep orange-red solution, and crystallises from the solution unchanged. The constitution of this salt is represented by the formula,

$$16WO_3.3V_2O_5.P_2O_5.5(NH_4)_2O + 37Aq,$$

as the following analyses show:

1.0379 gram lost on ignition with WO_4Na_2 0.1826 gram = 17.59 per cent. NH_3 and H_2O.

1.2811 gram gave 0.1264 gram NH_4Cl = 4.80 per cent. $(NH_4)_2O$.

1.0652 gram gave 0.1074 gram V_2O_5 = 10.08 per cent.

1.0130 gram gave 0.0419 gram $P_2O_7Mg_2$ = 2.64 per cent. P_2O_5.

The formula given requires:

		Calculated.		Found.	
$16WO_3$	3712	69.67	82.62	69.69	82.41
$3V_2O_5$	548	10.28		10.08	
P_2O_5	142	2.67		2.64	
$5(NH_4)_2O$	260	4.88		4.80	
$37H_2O$	666	12.50		12.79	
	5328	100.00		100.00	

Adopting the provisional hypothesis which I have proposed above, that V_2O_5 as $V_2O_2.O_3$ may partially replace MoO_3 or WO_3 in these combinations, and that, on the other hand, V_2O_5 also replaces P_2O_5, we may write the formula given above,

$$\begin{gathered}8WO_3.2V_2O_2.O_3.P_2O_5.3(NH_4)_2O + \\ 8WO_3.V_2O_5.2(NH_4)_2O.H_2O + 36Aq,\end{gathered}$$

in which formula the first term is reduced to the type of

$$10WO_3.P_2O_5.3(NH_4)_2O.$$

The presence of five molecules of ammonic oxide shows that the salt belongs to the acid type so often met with in this class of compounds, and upon the view which I consider probable,[1] that the formulas of all the phospho-tungstates and phospho-molybdates as now received should be doubled, we should write the above formula

$$16WO_3.2V_2O_2.O_3.V_2O_5.P_2O_5.5(NH_4)_2O.H_2O + 36Aq;$$

corresponding to

$$16WO_3.2P_2O_5.5(NH_4)_2O.H_2O.$$

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[1] Proceedings of the American Academy of Arts and Sciences, **17**, 89.

I consider this view of the subject as most probable in the present state of our knowledge.

60 : 3 : 2 *Series.*—When the 20 : 1 : 6 baric phospho-tungstate already described is boiled with vanadic hydrate, $VO(OH)_3$, the acid dissolves readily, and a beautiful orange-red solution is formed. On cooling, a salt separates in octahedral crystals, which have a very fine aurora-red color. The crystals dissolve rather easily in hot water, but are at the same time decomposed. A brownish orange salt then separates in distinct crystals, together with a white powder. The two can be separated mechanically. The mother liquor of the aurora-red salt yields on evaporation large dark-red crystals. Of the aurora-red salt,—

0.4165 gram lost on ignition with WO_4Na_2 0.0540 gram = 12.96 per cent.

1.1550 gram lost on ignition with WO_4Na_2 0.1500 gram = 12.98 per cent.

0.8819 gram gave of mixed oxides 0.6474 gram = 73.41 per cent.

1.4699 gram gave of mixed oxides 1.0784 gram = 73.37 per cent.

$\left\{\begin{array}{l}\text{1.5188 gram gave of mixed oxides 1.1145 gram = 73.38 per cent.}\\ \text{1.5188 gram gave of } P_2O_7Mg_2 \text{ 0.0508 gram = 2.14 per cent. } P_2O_5\end{array}\right.$

$\left\{\begin{array}{l}\text{1.0522 gram gave of mixed oxides 0.7709 gram = 73.26 per cent.}\\ \text{1.0522 gram gave of } P_2O_7Mg_2 \text{ 0.0380 gram = 2.31 per cent } P_2O_5\end{array}\right.$

1.3324 gram gave of V_2O_5 by titration 0.0258 gram = 1.93 per cent.

0.2693 gram gave of V_2O_5 by titration 0.0051 gram = 1.87 per cent.

The analyses correspond to the formula

$$60WO_3.3P_2O_5.2V_2O_5.18BaO + 144Aq,$$

which requires:

		Calculated.		Mean.					
$60WO_3$	13920	69.39	73.35	69.23	73.35	69.29	69.25	69.26	69.14
$3P_2O_5$	426	2.14		2.22		2.14	2.31		
$2V_2O_5$	366	1.82		1.90		1.93	1.87		
$18BaO$	2754	13.73		13.68			13.68		
$144H_2O$	2592	12.92		12.97		12.96	12.98		
	20058	100.00		100.00					

The baric oxide was determined by difference. In all determinations of the three acid oxides it was found necessary to ignite finally with a weighed quantity of normal sodic tungstate, in order to expel the mercuric oxide completely, and obtain a constant weight. The aurora-red salt may be regarded as a double compound, with the possible formula

$$3[12WO_3.P_2O_5.4BaO.2H_2O] + 2[12WO_3.V_2O_5.3BaO.3H_2O] + 132Aq.$$

It has, I believe, the highest molecular weight, 20058, yet observed, though I shall describe a little farther on a phospho-vanadio-vanadico-tungstate with the formula

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150Aq,$$

with the molecular weight 20066. It will be interesting to determine the specific heats of bodies of this class, as well as the heat of formation. The formation of the aurora-red salt is very simply expressed by the equation,

$$3[20WO_3.P_2O_5.6BaO] + 2V_2O_5 = 60WO_3.3P_2O_5.2V_2O_5.18BaO,$$

the process being one of simple addition.

I have mentioned above the fact that a dark red salt crystallises from the mother liquor of the aurora-red salt. The following analytical results were obtained with the small quantity of this salt at my disposal:

0.7660 gram gave 0.5570 gram mixed oxides = 72.71 per cent.
1.0405 gram gave 0.2133 gram SO_4Ba = 13.45 per cent. BaO.
1.0405 gram lost on ignition 0.1451 gram = 13.94 per cent.

In the orange-brown salt formed by the decomposition of the aurora-red salt,

1.1919 gram lost on ignition with WO_4Na_2 0.1611 gram = 13.51 per cent.
1.0476 gram gave 0.7653 gram mixed oxides = 73.05 per cent.
1.4122 gram gave 0.3078 gram SO_4Ba = 14.31 per cent.
1.2372 gram gave 0.0087 gram V_2O_5 = 0.70 per cent.

No formulas can be deduced from these analyses, but they may serve to identify the salts analysed in future investigations.

18 : 3 : 4 *Series.*—The 24 : 1 phospho-tungstate of sodium already described, $24WO_3.P_2O_5.2Na_2O.4H_2O + 23Aq$, is readily dissolved by boiling with a solution of ammonic meta-vanadate, and gives a deep orange-red liquid. This solution does not yield crystals on evaporation, or after standing for some time. When, however, a solution of potassic bromide is added in large excess, a deep orange-red crystalline precipitate is quickly formed in large quantity. The

salt exhibits the peculiar aurora-red tint which is often observed when phosphoric acid or a soluble phosphate is mixed with a solution containing both tungstic and vanadic oxides. The compound dissolves in a rather large proportion of hot water, but at the same time undergoes decomposition, and the solution after a time deposits a bright orange-brown crystalline salt without the peculiar aurora-red tint. The first-mentioned potassic salt, as precipitated from a cold solution, allowed to stand twenty-four hours, then washed with cold water and dried on woollen paper, gave on analysis the formula

$$18WO_3.4V_2O_5.3P_2O_5.8K_2O + 32Aq,$$

which may perhaps be written

$$2[6WO_3.2V_2O_5.P_2O_5.3K_2O] + 6WO_3.P_2O_5.2K_2O.H_2O,$$

the type of the first compound being

$$8WO_3.P_2O_5.3K_2O.$$

1.1017 gram lost on ignition with WO_4Na_2 0.0973 gram = 8.83 per cent.

1.0803 gram gave 0.8646 gram mixed oxides = 80.03 per cent.

1.1159 gram gave 0.1218 gram V_2O_5 = 10.91 per cent.

1.2104 gram gave 0.1227 gram $P_2O_7Mg_2$ = 6.48 per cent.

The formula given requires:

		Calculated.		Found.	
$18WO_3$	4176	62.68	80.06	62.64	80.03
$4V_2O_5$	732	10.99		10.91	
$3P_2O_5$	426	6.39		6.48	
$8K_2O$	752	11.29		11.14	
$32H_2O$	576	8.65		8.83	
	6662	100.00			

7 : 1 : 1 *Series.*—The bright orange-brown salt formed by the decomposition of the 18 : 4 : 3 salt was in small distinct granular crystals. Of this salt,

0.9773 gram lost on ignition with WO_4Na_2 0.0780 gram = 7.98 per cent.

1.0160 gram gave 0.8205 gram mixed oxides = 80.76 per cent.

1.3077 gram gave 0.1037 gram V_2O_5 = 7.93 per cent.

1.0113 gram gave 0.0958 gram $P_2O_7Mg_2$ = 6.06 per cent. P_2O_5.

The analyses correspond, though not very closely, to the formula

$$7WO_3.V_2O_5.P_2O_5.3K_2O + 11Aq,$$

which requires:

		Calculated.		Found.	
$7WO_3$	1624	66.86	80.23	66.67	80.76
V_2O_5	183	7.53		7.93	
P_2O_5	142	5.84		6.06	
$3K_2O$	282	11.61		11.26	
$11H_2O$	198	8.16		7.98	
	2429	100.00			

According to the view which I have taken as to the function of V_2O_5 in this class of compounds, the 7 : 1 : 1 potassic salt belongs to the type

$$8WO_3.P_2O_5.3K_2O,$$

$V_2O_2.O_3$ taking the place of one molecule of WO_3. A much more extended study will be necessary to test this hypothesis. The vanadio-phospho-tungstates are probably numerous, and from their great beauty, as well as from their theoretic interest, form an attractive subject for investigation. The following notes may serve to furnish fresh points of departure: When the solution of vanadio-tungstate of sodium (obtained by boiling 12 : 5 acid sodic tungstate with the mixed oxides of vanadium and oxidising completely with bromine) is mixed with a solution of hydro-disodic phosphate, no apparent action takes place; but on boiling, the orange solution takes a deep red color, and soon deposits splendid ruby-red crystals in quantity. These crystals are decomposed in part even by cold water, which appears to separate phosphoric acid or sodic phosphate. An orange-colored sodium salt then separates. Almost exactly the same results are obtained when a solution of vanadio-tungstate of ammonium is boiled with a solution of ammonic phosphate. The liquid takes a beautiful deep red tint, and soon deposits splendid ruby-red crystals. The solution of the sodium salt, after a day or two, gives with one of trimethyl-ammonium chloride, $N(CH_3)_3HCl$, very fine granular ruby-red crystals. Of these crystals,

0.9752 gram gave 0.8549 gram mixed oxides = 87.66 per cent.
1.1543 gram gave 0.0631 gram V_2O_5 = 5.46 per cent.
1.0061 gram gave 0.0552 gram $P_2O_7Mg_2$ = 3.51 per cent.

The loss corresponding to water and trimethyl-ammonium oxide is 12.34 per cent. The ratio of the three oxides, WO_3, V_2O_5, and P_2O_5, is $34WO_3.3V_2O_5.2P_2O_5$; but the determination of the trimethyl ammonium oxide will be necessary in order to settle the formula completely. I am indebted to the kindness of Prof. Arthur Michael for a supply of the trimethylamin salt, which has proved of great service to me. The disposition of the corresponding oxide to form well-crystallised salts makes it a valuable test, and it should become an article of commerce for chemists' use.

VANADIO-VANADICO-MOLYBDATES.

The salt about to be described constitutes the type of a new and extensive series of complex acids, which contain two different linking oxides, embraced respectively under the formulas R_2O_5 and $R'O_2$, in which, however, R and R′ may be identical. The general formula for this class of molybdenum compounds may be written

$$m\mathrm{MoO_3}.n\mathrm{R_2O_5}.p\mathrm{R'O_2}.x\mathrm{R''_2O},$$

which, in the case of the identity of R and R′, becomes

$$m\mathrm{MoO_3}.n\mathrm{R_2O_5}.p\mathrm{RO_2}.x\mathrm{R''_2O}.$$

I shall show that there are corresponding salts containing tungsten in place of molybdenum. Vanadio-vanadico-molybdates are very readily formed by boiling a mixture of the two oxides of vanadium with an acid molybdate; by the partial reduction of vanadio-molybdates; or by digesting solutions of acid molybdates with solutions which contain vanadic dioxide and pentoxide.

28:4:1 *Vanadio-vanadico-molybdate of Ammonium.*—When pure ammonic divanadate is ignited in an open platinum vessel, and the remaining mass is boiled with an excess of a solution of 14:6 acid ammonic molybdate, a greenish solution is formed, which after filtration and evaporation yields on cooling a pale greenish-yellow crystalline salt. After draining on the filter-pump, the salt may be redissolved and recrystallised, when it presents very distinct granular greenish-yellow crystals. The solution is bright yellow. Of this salt,

1.4613 gram lost on ignition with WO_4Na_2 0.2527 gram = 17.29 per cent.

1.3326 gram gave by titration 0.1423 gram $(NH_4)_2O$ = 10.68 per cent.

1.2031 gram gave by titration 0.1288 gram $(NH_4)_2O = 10.71$ per cent.

2.1968 grams gave 0.2184 gram $V_2O_5 = 9.95$ per cent. $VO_2 + V_2O_5$.

0.9980 gram gave 0.0607 gram $VO_2 = 6.08$ per cent. VO_2.

The analyses lead to the formula

$$28MoO_3.4V_2O_5.VO_2.11(NH_4)_2O + 20Aq,$$

which requires:

		Calculated.	Found.
$28MoO_3$	4032	73.56	73.34
$4VO_2$	334	6.09	6.08
V_2O_5	183	3.34	3.29
$11(NH_4)_2O$	572	10.44	10.68 10.71
$20H_2O$	360	6.57	6.60
	5481	100.00	

The compound is doubtless to be regarded as a double salt, but there are at present no data upon which to base even a conjectural arrangement. The salt is slightly soluble in cold water, the solution being strongly acid to litmus paper. It is soluble in hot water, and separates from the solution without sensible decomposition. The solution is reduced with great difficulty, either by sulphurous oxide or by sulphydric acid gas. For analysis I found it best, after oxidation with nitric acid, to boil with excess of ammonia, evaporate with ammonic chloride, and separate the ammonic meta-vanadate upon an asbestos filter. The vanadium was then determined by titration with hypermanganate. The vanadic dioxide was determined by hypermanganate in the solution of the salt, after adding phosphoric and sulphuric acids. It was found necessary to use very dilute solutions, and the close agreement of the determination of vanadic dioxide with the formula cannot be regarded as other than accidental. The reactions of this salt are as follows: the cold dilute solution gives no precipitate with salts of zinc, copper, manganese and cadmium; a pale yellow flocky precipitate with baric chloride, which soon becomes granular-crystalline; with potassic bromide, after some days, very fine, large prismatic crystals; with argentic nitrate, the solution gives a flocky precipitate, which is yellow with a tinge of buff; with mercurous nitrate, a bright, and with thallous nitrate, a pale yellow, flocky precipitate.

15 : 1 : 2 *Vanadio-vanadico-molybdate of Barium.*—Baric chloride added to the mother liquor from which the preceding salt was prepared gave a pale yellow crystalline, and, so far as could be seen, homogeneous precipitate in very small grains. This was filtered off, well washed with cold water, and dried on woollen paper for analysis. The filtrate was greenish, and gave no other salt on evaporation. The barium salt is very slightly soluble in cold water, and is decomposed by boiling water, with separation of baric molybdate, and formation of a pale greenish-yellow solution, which possibly contains a new salt of the same class. The salt is decomposed by boiling with mercurous nitrate, giving a bright yellow crystalline body. Boiled with argentic nitrate it gives an orange-colored precipitate which is also crystalline. Of this salt,

1.1690 gram gave 0.7260 gram $WO_3 + V_2O_5 + VO_2 = 62.09$ per cent. and 0.4772 gram $SO_4Ba = 26.80$ per cent. BaO.

1.5526 gram gave 0.6332 gram $SO_4Ba = 26.70$ per cent. BaO.

1.0341 gram lost on ignition 0.1127 gram = 10.90 per cent. H_2O.

2.1990 grams gave by titration 0.1748 gram = 7.95 per cent. V_2O_5

The titration was effected by $SO_4H_2 + SO_4(NH_4)_2 + 6Aq$ in a solution to which HCl had been added, after oxidation with nitric acid and addition of an excess of sodic carbonate. All the vanadium present was therefore estimated as V_2O_5.

The analyses correspond closely to the formula

$$30MoO_3.2V_2O_5.3VO_2.14BaO + 48Aq,$$

which requires:

		Calculated.	Found.	
$30MoO_3$	4320	54.40	54.40 (diff.)	
$2V_2O_5$	366	4.62	4.73	
$3VO_2$	249	3.13	3.22	
$14BaO$	2142	26.97	26.70	26.80
$48H_2O$	864	10.88	10.90	
	7941	100.00		

The compound is doubtless a double salt, and its formula may perhaps be

$$2[6MoO_3.V_2O_5.4BaO.2H_2O] + 3[6MoO_3.VO_2.2BaO.4H_2O] + 32Aq;$$

only it must be remarked that the empirical formula given above must be doubled in order to obtain a symmetrical structural formula, as the number of molecules of vanadic dioxide is uneven in the simpler expression given.

VANADIO-VANADICO-TUNGSTATES.

The class of salts to which I have given this name come also under the general formula

$$m\mathrm{RO_3}.n\mathrm{R'_2O_5}.p\mathrm{R''O_2}.x\mathrm{R'''_2O},$$

and constitute, like the corresponding compounds containing molybdenum, a new ternary series. They are formed under the same conditions as these last, and like these have an orange or orange-red color, with a more or less distinct tinge of green.

12 : 2 : 3 (?) *Vanadio-vanadico-tungstate of Sodium.*—This salt, which was the first which I obtained containing vanadium, was formed by boiling with 12 : 5 acid sodic tungstate, a commercial vanadic pentoxide, which I owed to the kindness of Dr. J. Lawrence Smith, and which was probably prepared by igniting ammonic meta-vanadate, and therefore contained a certain proportion of vanadic dioxide. I did not succeed in preparing it a second time with a new preparation of the mixed oxides, and therefore trust that the incomplete analyses and meagre description of this and the corresponding ammonium and silver salts will be excused. The solution of the mixed oxides in the acid tungstate gave a deep orange-red solution, which, on evaporation to the consistency of a syrup, yielded after a time large orange-red apparently triclinic crystals, extremely soluble in water, and crystallising only from syrupy solutions. In this salt twice recrystallised,

0.5968 gram lost on ignition to fusion of the residue 0.1019 gram = 17.07 per cent.

0.6852 gram lost on ignition to fusion of the residue 0.1164 gram = 16.98 per cent.

0.3311 gram gave 0.2481 gram $\mathrm{WO_3 + V_2O_5 + VO_2} = 74.96$ per cent.

These analyses taken in connection with those of the ammonium and silver salts, may, with at least a certain degree of probability, be considered as leading to the formula

$$\mathrm{12WO_3.2V_2O_5.3VO_2.6Na_2O + 43Aq},$$

which requires:

		Calculated.	Found.	
$12WO_3$	2784	74.79	74.96	
$2V_2O_5$	366			
$3VO_2$	249			
$6Na_2O$	372	8.18	8.05	
$43H_2O$	774	17.03	16.99	17.07
	4545	100.00		

The solution of this salt had a deep orange-red color with distinct greenish reflections. Bromine water instantly gave a very fine deep orange solution, having nearly the color of potassic dichromate, and without the greenish tint: the liquid then contained only a sodic vanadio-tungstate. The solution gave flocky precipitates with various salts of heavy metallic oxides, and a bright red crystalline precipitate with argentic nitrate. A solution of acid potassic tungstate dissolved the mixture of oxides of vanadium, forming a greenish-orange solution, which also became bright orange-red with bromine. The potassic salt crystallised from this solution after evaporation to the consistency of a syrup, and gave crystals of peculiar greenish-orange tint. The solution of this salt gave a bright orange indistinctly crystalline precipitate with mercurous nitrate. This precipitate was decomposed by dilute chlorhydric acid, yielding a yellow solution from which no crystals were obtained by evaporation. This is perhaps the acid of the series.

12 : 2 : 3 (?) *Ammonium Salt.*—12 : 5 acid ammonic tungstate was boiled with a portion of the same commercial vanadic oxides in excess. The oxides dissolved readily, leaving, as in the cases of the sodium and potassium salts, a quantity of a black insoluble powder. The deep orange-yellow solution deposited on cooling beautiful orange-colored crystals of an ammonium salt; but on evaporating the main solution *in vacuo*, two kinds of crystals were obtained, one in relatively large dark-red octahedrons, the other much lighter-colored and resembling potassic dichromate. The darker salt gave in two analyses 17.98 and 18.05 per cent. of water and ammonic oxide. Of the lighter-colored salt separated mechanically from the first-named,

0.8429 gram lost on ignition 0.1149 gram = 13.63 per cent. H_2O and NH_3.

0.8164 gram lost on ignition 0.1107 gram = 13.56 per cent. H_2O and NH_3.

0.9047 gram gave 0.1502 gram NH_4Cl = 8.07 per cent. $(NH_4)_2O$.

The analyses agree, so far as they go, very well with the formula,

$$12WO_3.2V_2O_5.3VO_2.6(NH_4)_2O + 12Aq,$$

which requires:

		Calculated.	Found.
$12WO_3$	2784	86.55	86.41 (diff.)
$2V_2O_5$	366		
$3VO_2$	249		
$6(NH_4)_2O$	312	7.94	8.07
$12HO_2$	216	5.51	5.52
	3927	100.00	

The solution of this salt gives a beautiful scarlet precipitate with argentic nitrate, and a fine yellow precipitate with salts of strychnin, which after standing some hours becomes granular crystalline.

12 : 2 : 3 (?) *Vanadio-vanadico-tungstate of Silver.*—The salt analysed was in beautiful scarlet crystals, and was prepared by precipitating the ammonium salt with argentic nitrate, and washing with cold water. The salt is not distinctly crystalline when first thrown down, but becomes so after standing in the liquid. It is very slightly soluble in cold water, but dissolves in much hot water to a yellow liquid. Of this salt,

2.1193 grams lost on ignition 0.0621 gram = 2.93 per cent.

0.7511 gram gave 0.7420 gram AgCl = 28.21 per cent. Ag_2O.

These analyses agree with the formula,

$$12WO_3.2V_2O_5.3VO_2.6Ag_2O + 8Aq,$$

which requires:

		Calculated.	Found.
$12W_2O_3$	2784	68.87	68.86 (diff.)
$2V_2O_5$	366		
$3VO_2$	249		
$6Ag_2O$	1392	28.21	28.21
$8H_2O$	108	2.92	2.93
	4935	100.00	

The analyses which I have given may not be considered as sufficiently complete to establish the formulas assigned, but they serve to prove the existence of at least one class of vanadio-vanadico-tungstates. In substances of such high molecular weights the agreement between the formulas of three different salts prepared under precisely the same conditions has a certain value, but it is less conclusive than when the molecular weight is lower, because such a change as is produced by writing, for instance, $2VO_2$ for V_2O_5, does not greatly affect the percentage results. If we admit the correctness of the formulas given, it will still be necessary to double them in order to construct a structural formula which shall be symmetrical, since the number of molecules of VO_2, either free or contained in V_2O_5, is uneven. For the complete analysis of compounds of this class it will be most advantageous to determine the vanadic pentoxide by heating with strong chlorhydric acid in the manner already indicated, and then to determine the dioxide in another portion by means of hypermanganate, if possible, or by first oxidising with bromine, and then determining the whole of the vanadium as pentoxide by boiling with chlorhydric acid and titrating as before.

PHOSPHO-VANADIO-VANADICO-TUNGSTATES.

I have given this rather ponderous appellation to a class of compounds in which vanadium exists partly as pentoxide and partly as dioxide. They may be regarded simply as double salts, but in the present state of our knowledge it will be found most convenient to consider them as a special class.

Salts of this type are formed whenever phospho-tungstates are mixed with vanadates in presence of vanadic dioxide, when vanadio-vanadico-tungstates are heated with solutions of alkaline phosphates or with phosphoric acid, and when phospho-vanadates and alkaline tungstates are brought together in presence of a reducing agent and of an acid. The salts are sometimes green and sometimes orange-red. In the last case they have frequently the peculiar aurora-red tint noticed among the colors of the phospho-vanadio-tungstates. They pass readily by oxidation with bromine or nitric acid into salts of the last-mentioned type, and they may be also derived from these by a partial reduction of the vanadic pentoxide.

Analytical Methods.—These are essentially the same as those which have been described. All the non-basic oxides may be determined together by means of mercurous nitrate and mercuric oxide, after complete oxidation with nitric acid. Phosphoric oxide may usually be determined directly, or after separation of a non-alkaline base, by double precipitation with magnesia mixture. The vanadic pentoxide can be estimated by boiling with chlorhydric acid and titration in the manner already pointed out. To determine the vanadic dioxide the solution must first be oxidised completely, so as to convert the dioxide into pentoxide, any excess of the oxidising agent employed being carefully removed. I prefer to use bromine water for this purpose. The whole of the vanadium may then be determined by titration as above. The difference between the amount of vanadic pentoxide found before and after complete oxidation then gives, by a simple proportion, the corresponding amount of vanadic dioxide. It must be remembered that the sum of the non-basic oxides found by the mercury process requires to be corrected by adding the amount of oxygen required to convert the vanadic dioxide present into the equivalent of pentoxide. When the whole quantity of vanadium present is small, this correction may be neglected, as falling within the limits of the errors of analysis unavoidable with our present methods. Baric oxide in these salts is best estimated by difference, as the direct estimation almost always gives too high a percentage.

60 : 3 : 1 : 1 *Barium Salt.*—When ammonic vanadate is heated in a porcelain crucible until all the ammonia is expelled, the greenish residue consists, as already stated, chiefly of a mixture of vanadic dioxide and pentoxide. If this mixture be added in small portions at a time to a boiling solution of the baric phospho-tungstate, $20WO_3.P_2O_5.6BaO$, already described, the liquid takes at once a rather dull green color. The filtrate from the excess of mixed oxides, after evaporation in a water-bath and standing for some hours, yields a mass of deep green crystals, mechanically mixed with a relatively small proportion of a fine white powder, which may easily be removed by washing with cold water and pouring off the powder in suspension. The dark green crystals are regular octahedrons, frequently in long aggregates and beautifully defined. The salt is rather insoluble in cold but readily soluble in hot water, with a dark and rather dull green color. The cold solution, after adding dilute sulphuric acid, is not sensibly oxidised by potassic hypermanganate or in alkaline solution by iodine. The hot solution is oxidised by bromine and by nitric acid, and becomes deep orange-red. At a boiling heat potassic hypermanganate also oxidises it, the quantity required for oxidation being very small, so that it can with difficulty be estimated. Of this salt,

1.2596 gram gave 0.9178 gram mixed oxides = 72.86 per cent.
1.0160 gram lost on ignition 0.1362 gram = 13.40 per cent.

1.4649 gram lost on ignition 0.1969 gram = 13.44 per cent.
1.8580 gram gave 0.0624 gram $P_2O_7Mg_2$ = 2.15 per cent. P_2O_5.
1.3846 gram gave 0.0105 gram V_2O_5 = 0.76 per cent.
1.1972 gram gave 0.0131 gram V_2O_5 = 1.09 per cent.

In these analyses the vanadic pentoxide was determined directly in the salt, by boiling with chlorhydric acid and titrating. In two other analyses the vanadic dioxide was first completely oxidised by means of bromine; the whole quantity of vanadium was then determined as before. The percentage of vanadic dioxide was then calculated from the exces of V_2O_5 over that found by direct analysis. In this process,

1.1379 gram gave 0.0161 gram V_2O_5 = 1.44 per cent.
1.1714 gram gave 0.0200 gram V_2O_5 = 1.71 per cent.

The analyses correspond very closely to the formula,

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150Aq,$$

which requires:

		Calculated.	Found.	
$60WO_3$	13920	69.37	69.32	
$3P_2O_5$	426	2.12	2.15	
V_2O_5	183	0.92	1.09	0.76
VO_2	83	0.42	0.46	
$18BaO$	2754	13.72	13.72	
$150H_2O$	2700	13.45	13.40	13.44
	20066	100.00		

The baric oxide is estimated by difference. The relation of this salt to the aurora-red octahedral phospho-vanadio-tungstate of barium already described is interesting. We have respectively the formulas,

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150Aq,$$
$$60WO_3.3P_2O_5.V_2O_5.V_2O_5.18BaO + 144Aq,$$

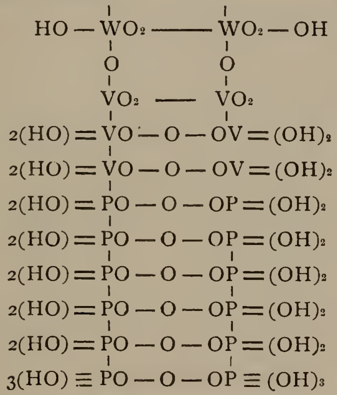
and it is easy to see how, at least theoretically, one salt could be prepared from the other. With respect to the rational constitution of the green salt, it is possible at present only to form a provisional hypothesis. I am disposed to regard it as a triple compound, and to assign to it the formula,

$$3[12WO_3.P_2O_5.3BaO.3H_2O] + 12WO_3.V_2O_5.5BaO.H_2O + 12WO_3.VO_2.4BaO.$$

In this formula all the terms correspond to known compounds, the last to the dodeka-silico-tungstate type established by Marignac, VO_2 replacing SiO_2. Of course, as in similar cases, various other formulas may be proposed. I lay no particular stress upon the view I have taken, which a wider and deeper study of these compounds may prove to be untenable. The formation of the salt may be expressed by the equation,

$$3[20WO_3.P_2O_5.6BaO] + V_2O_5 + VO_2 = 60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO.$$

The formula must be doubled to permit of a representation by means of a symmetrical structural formula. If we omit all the molecules of tungstic oxide except two, in order to save space, the linking portion of the structural formula of the corresponding acid may be written as follows:



$$\begin{array}{rcccl}
 & | & & | & \\
HO - & WO_2 & \text{———} & WO_2 & - OH \\
 & | & & | & \\
 & O & & O & \\
 & | & & | & \\
 & VO_2 & \text{——} & VO_2 & \\
 & | & & | & \\
2(HO) = & VO & - O - & OV & = (OH)_2 \\
 & | & & & \\
2(HO) = & VO & - O - & OV & = (OH)_2 \\
 & | & & & \\
2(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & & \\
2(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
2(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
2(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
2(HO) = & PO & - O - & OP & = (OH)_2 \\
 & | & & | & \\
3(HO) \equiv & PO & - O - & OP & \equiv (OH)_3
\end{array}$$

This formula, which, like most of those which I have given, is purely conjectural, will at least serve to show how the two different states of oxidation of vanadium may be represented in the combination, and how the basicity of PO and VO may be affected by their position. Such formulas are not without value, as suggesting the possibility of forming new combinations, even if, as I prefer in this case to do, we consider the salt represented as double or triple. Structural formulas for double and still more for triple inorganic salts would probably be still more complex, and what I have aimed at is to show how all the valences may be satisfied in an arbitrarily selected compound containing four oxides of three different types.

The general results deducible from the formulas which I have given in the present instalment of my work are as follows:

1. Hypophosphorous and phosphorous acids may enter into combination with tungstic and molybdic oxides as links, so as to form complex inorganic acids. The structure of these four classes of acids indicates the possibility of forming new series of acids, in which methyl and other organic radicals or residues may take the place of the constitutional hydrogen of the hypophosphorous and phosphorous linking terms, and again of others in which, besides the replacement of hydrogen, phosphorus may be replaced by arsenic, and possibly by antimony and other elements.

2. Vanadium may replace phosphorus and arsenic so as to form well-defined series of vanadio-molybdates and vanadio-tungstates embraced under the general formula,

$$m\mathrm{RO_3}.n\mathrm{V_2O_5}.p\mathrm{R'_2O}.$$

3. Vanadic and phosphoric pentoxides may enter simultaneously into combination with tungstic or molybdic oxide, so as to form classes of triple acids embraced under the general formula,

$$m\mathrm{RO_3}.n\mathrm{P_2O_5}.p\mathrm{V_2O_5}.v\mathrm{H_2O}.$$

4. A class of quadruple acids exists into which, in addition to phosphoric and vanadic pentoxides, vanadic dioxide may enter, the general formula being

$$m\mathrm{RO_3}.n\mathrm{P_2O_5}.p\mathrm{V_2O_5}.r\mathrm{VO_2}.v\mathrm{H_2O}.$$

5. In another class of ternary or triple acids molybdic or tungstic oxide may be combined with both vanadic pentoxide and vanadic dioxide, the general formula being

$$m\mathrm{RO_3}.n\mathrm{V_2O_5}.p\mathrm{VO_2}.v\mathrm{H_2O}.$$

I shall show hereafter that all of these results are capable of further generalisation ; that, for example, other oxides of the types $\mathrm{RO_2}$ corresponding to hydrates of the form $\mathrm{R(OH)_4}$ may replace $\mathrm{VO_2}$ or $\mathrm{V(OH)_4}$; that other pentoxides may replace $\mathrm{P_2O_5}$, $\mathrm{As_2O_5}$, and $\mathrm{V_2O_5}$, either in the presence or in the absence of oxides of the type $\mathrm{RO_2}$; in short, that the complex inorganic acids form a new department of inorganic chemistry, and not a series of isolated compounds.

(*To be continued.*)

EXPERIMENTS ON THE ESTIMATION OF LEAD AS LEAD DIOXIDE BY MEANS OF THE ELECTRIC CURRENT.

By Frank Tenney.

These experiments were undertaken to investigate anew the practicability of the determination of lead as lead dioxide in acid solution. The first experiments in this direction were made by Luckow[1] and by May.[2] May used a solution containing copper and 2½ per cent. of free nitric acid (calculated as anhydrous HNO_3), and obtained in this solution satisfactory results, weighing the lead as lead monoxide, into which the dioxide was converted by heat. Luckow[3] says: "The complete precipitation of the lead occurs only in the presence of at least 10 per cent. of free nitric acid, if only lead be present. If the solution contain copper also, less free acid is required. With less than 8 per cent. free nitric acid, lead is liable to be thrown down on the negative pole with the copper as metal."

Riche[4] proceeds in the same way as Luckow, but warms the solution to 60°–90°. The work of Parodi and Mascazzini[5] in solutions containing tartrates, and of Classen and von Reis[6] in oxalate solutions, relates to the precipitation of metallic lead, and has therefore little connection with the present subject.

The substance used for analysis in the present experiments was lead nitrate, whose purity was proved by estimating the lead. This was done by igniting the lead nitrate and weighing the residual oxide, PbO.

Two determinations gave:

	I.	II.	Theory requires.
Weight PbN_2O_6 taken	0.8005	0.9713	
Weight PbO found	0.5395	0.6542	
Per cent. of Pb	62.54	62.54	62.54

A solution was made of this lead nitrate containing 1.4690 gram to the litre, and 25 cc. of this solution were taken each time for analysis. Of this solution, 25 cc. should yield 0.0266 gram dioxide.

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[1] Zeitschrift für analytische Chemie, **11** (1872), 9-12; **19** (1880), 1.

[2] American Journal of Science, [3] **6**, 255.

[3] Zeitschrift für analytische Chemie, **19**, 15.

[4] Annales de Chimie et de Physique, [5] **13**, 508.

[5] Zeitschrift für analytische Chemie, **18**, 588.

[6] Berichte der deutschen chemischen Gesellschaft, **14**, 1622.

In a neutral solution the lead was deposited partly as metallic lead on the negative, and partly as lead dioxide on the positive electrode. Three portions of the solution were then taken, and to No. I 1½ per cent. of free nitric acid (calculated as anhydrous HNO_3), to No. II 5 per cent., and to No. III 10 per cent. were added. After 16 hours' action of the current the amount of lead dioxide thrown down was found to be:

I.	II.	III.	Calculated.
0.0216	0.0253	0.0265	0.0266

The coating on No. I was not strongly adherent.

In the next trial, No. I received 10 per cent., No. II 13⅓ per cent., No. III 16⅔ per cent. of free nitric acid; the results were:

I.	II.	III.	Calculated.
0.0266	0.0274	0.0272	0.0262

In the next trial 50 cc. solution of lead nitrate were taken and 10 per cent. of free acid added. The results were:

I.	II.	III.	Calculated.
0.0533	0.0533	0.0452	0.0532

In No. III, owing to irregularity of the current, the dioxide came down unequally and scaled off badly.

A solution of copper containing 0.2920 gram copper in 25 cc. was made up, and three portions, each containing 25 cc. of this solution and 25 cc. of the lead solution, were subjected to the action of the current after adding to No. I 1½ per cent., to No. II 5 per cent., and to No. III 10 per cent. of free nitric acid. The results were:

I.		II.		III.		Calculated.	
PbO_2.	Cu.	PbO_2.	Cu.	PbO_2.	Cu.	PbO_2.	Cu.
0.0278	0.2967	0.0281	0.2924	0.0275	0.2930	0.0266	0.2920

The copper was in all cases slightly black.

In presence of iron with 1½ per cent., 5 per cent. and 10 per cent. of free acid the results were:

	I.	II.	III.	Calculated.
PbO_2	0.0261	0.0259	0.0200	0.0266

The last one scaled off badly, thus accounting for the low result. The electrodes used had areas of 73.13, 75.19 and 66.49 square centimeters respectively.

To sum up, one may say this method is reliable where the amount of lead is not too large and where there is a sufficient amount of free nitric acid present. Where the lead does not exceed 0.02 gram it may be thrown down as lead dioxide and weighed on ordinary flat electrodes. Where larger amounts are present, aliquot parts of a solution must be taken, or a platinum dish may be made the positive pole and the dioxide washed by decantation.

Since these experiments were made this method has been largely used in this laboratory for the estimation of lead in galena and in slags and mattes. From 10 per cent. to 20 per cent. of free nitric acid should be present; if there is too much, the lead dioxide, as fast as it is thrown down, redissolves in the nitrous acid resulting from the decomposition of the strong nitric acid. In slags and mattes the most satisfactory method is found to be as follows: After decomposition in the usual way, the lead and copper are precipitated as sulphides with sulphuretted hydrogen, these sulphides are dissolved in nitric acid, and the solution put in the circuit. A perfect and complete separation of the lead and copper is obtained. The small amount of sulphuric acid formed by the solution of the sulphides in nitric acid does not affect the accuracy of the determination.

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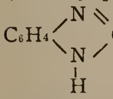
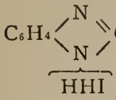
A NITRILE OF ANHYDRO-BENZDIAMIDO-BENZENE.

By Jas. Lewis Howe.

When the so called anhydro-benzdiamido-benzene of Hübner,[1] (Benzenyl-phenylene-amidine of Beilstein[2]) of the formula



$C_6H_4\left\langle\begin{matrix}N\\ \underset{H}{N}\end{matrix}\right\rangle C.C_6H_5$, is heated in a closed tube with an excess of cyanogen iodide, CNI, and a considerable quantity of benzene, a reaction takes place slowly at slightly below 100° C., and the tube becomes lined with dark red crystals of the triiodide of the anhydro-base,  $C_6H_4\left\langle\begin{matrix}N\\ \underbrace{N}_{HHI}\end{matrix}\right\rangle C.C_6H_5I_2$, while the benzene leaves upon evaporation a dark crystalline mass. This is for the most part soluble in hot petroleum ether (of boiling point 60°–70° C.), out of which it crystallises in small, lustrous, lemon-yellow tables, approximately hexagonal in shape. These melt at 105.5° C. (corrected), and analysis shows them to have the formula $C_{13}H_9N_2CN$, showing that a hydrogen atom of the anhydro-base has been replaced by the group CN. The analyses are as follows:

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[1] Annalen der Chemie, **208**, 302.

[2] Beilstein, Handbuch der Organischen Chemie, 2049.

I. 0.1880 gram gave 0.5277 gram CO_2 and 0.073 gram H_2O.

II. 0.2488 gram gave 0.7041 gram CO_2 and 0.111 gram H_2O.

III. 0.28 gram gave 0.7845 gram CO_2 and 0.1155 gram H_2O.

IV. 0.1643 gram gave at 9° C. and 768 mm. pressure 26 ccm.= 0.0316 gram N.

V. 0.1965 gram gave at 17.5° C. and 771 mm. pressure 32 ccm. =0.0376 gram N.

VI. 0.15 gram gave at 5° C. and 768 mm. pressure 23 5 ccm.= 0.029 gram N.

Calculated for $C_{14}H_9N_3$.		Found. I & V.	II & IV.	III & VI.
C	76.71	76.55	77.17	76.41
H	4.11	4.31	4.46	4.58
N	19.18	19.13	19.24	19.37

This nitrile is very stable, not decomposing at a very high temperature; it distils slowly with steam, and may in this way be obtained in a pure state, showing scarcely a trace of yellow color. It is easily soluble in alcohol, cold benzene, and hot petroleum ether; very slightly soluble in cold petroleum ether, and insoluble in water; in chloroform, glacial acetic acid and acetone it is exceedingly soluble. It crystallises out of benzene and alcohol in large needles; no crystals could be obtained from any of the above solutions suitable for crystallographical investigation.

In order to determine if possible which hydrogen atom was replaced by the CN group, I endeavored to change this group into the carboxyl; but in this I did not succeed.

By boiling the nitrile in a solution of caustic potash in water it was dissolved, ammonia given off, and from the solution a white precipitate was thrown down by hydrochloric acid, which dissolved in excess of the acid, and was again precipitated by ammonia. This precipitate was found to be the original anhydro-base, and the reaction may have been

$$C_{13}H_9N_2CN + KOH + HOH = NH_3 + C_{13}H_9N_2COOK,$$

followed immediately by the decomposition,

$$C_{13}H_9N_2COOK + KOH = K_2CO_3 + C_{13}H_{10}N_2;$$

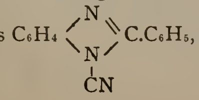
or, possibly,

$$C_{13}H_9N_2CN + KOH = C_{13}H_9N_2H + CONK,$$

and $$CONK + KOH + HOH = K_2CO_3 + NH_3.$$

In a second case the nitrile was gradually heated with water in a closed tube to 250° C. The greater part remained unchanged, but a small portion was decomposed into the original anhydro base, and the odor of the ammonia formed could be detected.

Claisen's method was also tried; but this was also unsuccessful. Hydrochloric acid gas was led into concentrated hydrochloric acid, which was kept in a freezing mixture until the acid became as concentrated as possible. In this a portion of the nitrile was placed, and allowed to remain twenty-four hours at a temperature considerably below 0° C. The nitrile dissolved very gradually; but from the solution only the hydrochloric acid salt of the anhydro base was obtained.

I further attempted to convert the CN group into the methylene-amine group, CH_2NH_2, by the use of sodium amalgam and water. In this case also the CN group was removed and the anhydro base alone obtained. It would, therefore, seem that the CN group replaces the hydrogen of the imine group. Were this not the case we should expect the formation of isomers; but there was in the tubes after heating no trace of any compound derived from the anhydro-base, except the nitrile and the triiodide. Further, were the CN group connected directly with a carbon atom of either o the benzene radicals, it would in all probability give an acid and an amine. On the contrary, the CN seemed to be easily separated from the rest of the molecule, as we should expect in case it were attached to a nitrogen atom. Hence, the probable formula of the nitrile is  $C_6H_4\left<\begin{matrix}N\\N\\|\\CN\end{matrix}\right>C.C_6H_5$, and its formation is expressed thus,

$C_{13}H_{10}N_2 + ICN = C_{14}H_9N_3 + HI$. A part of the hydriodic acid forms a salt of the anhydro-base, and the rest is decomposed into hydrogen and iodine, the latter uniting with the above salt to form a triiodide,

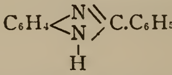
$$4C_{13}H_{10}N_2 + 3ICN = 3C_{14}H_9N_3 + C_{13}H_{11}N_2I_3 + H_2.$$

This compound is thus probably a cyanamide—anhydro-benzdiamido-benzene cyanamide—but, unlike most of these, it shows no tendency to polymerise. I shall hope soon to be able to make and study one or more of the isomers of this compound, in which the CN group shall be attached to one of the benzene radicals.

Brooks Laboratory, Cleveland, O., *May*, 1883.

THE ETHYL DERIVATIVES OF ANHYDRO-BENZDIAMIDO-BENZENE.

By Jas. Lewis Howe.

For some years past the action of various alkyl iodides upon the so-called anhydro-bases of Hübner has been studied in the chemical laboratory at Göttingen.[1] The base which has been most studied is anhydro-benzdiamido-benzene, the benzenyl-phenylene-amidine of Beilstein;[2] of the formula  $C_6H_4<\begin{matrix}N\\ \underset{\overset{|}{H}}{N}\end{matrix}>C.C_6H_5.$ When this is heated for several hours in a closed tube with an alkyl iodide at a temperature from 150° to 260° C., a dialkyl triiodide is generally formed of the formula $R''N(C_xH_y)_2I_3$, and this by treatment with lead hydroxide and afterward with potassium hydroxide, gives a hydroxide, $R''N(C_xH_y)_2OH$, which possesses more strongly basic properties than the anhydro-base. In a few instances where the heat used was rather low, the hydriodic acid salt of a monoalkyl base, $R''N.C_xH_y.HI$, has been formed; but the formation of this monoalkyl base seems to be, however, rather the result of chance than of any definite conditions. Hence it seemed desirable to study these relations more closely, and this paper is a resumé of the results obtained with ethyl iodide.

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[1] Annalen der Chemie, **210**, 328.

[2] Beilstein: Handbuch der Organischen Chemie, 2049.

Finely powdered anhydro-benzdiamido-benzene in quantities of about five grams was heated with an excess of ethyl iodide in a closed tube, at the lowest temperature at which a complete reaction took place. No pressure was noticed upon opening. When heated for twenty-four hours at 120° C. the tube contained for the most part straw-colored crystals, there being present but small quantities of the dark red crystals of the triiodides. The straw-colored crystals were found to consist of approximately equal parts of the iodide of the diethyl derivative and the hydriodic acid salt of the anhydro-base. No trace of a monoethyl derivative was in any instance to be detected.

The separation of the above salts by crystallisation is very difficult, but the bases may be easily separated by treating the aqueous solution of the iodides with soda, which precipitates completely the anhydro-base. After boiling, this is easily filtered off, and the diethyl hydroxide is precipitated by caustic potassa, its salts being decomposed only by the caustic alkalies. The following is a description of the base and several of its salts.[1]

Diethyl-anhydro-benzdiamido-benzene hydroxide (*Benzenyl-diethyl-phenylene-amidine of Beilstein*).—Melting point, 136° C. (corrected); crystallises in colorless monoclinic prisms, consisting of the faces ∞P and oP. The angle of the principal axis is very much inclined, but owing to the oP face being in no case smooth, it was impossible to determine the angle accurately. The crystals were also too brittle for optical investigation. It is insoluble in water and the alkalies, difficultly soluble in petroleum ether, easily in cold alcohol, ether, and acetone, and especially soluble in benzene and chloroform. It dissolves readily in dilute acids, forming salts, and from the solution of these it is reprecipitated by caustic alkalies.

Analyses:

I. 0.3260 gram gave 0.9175 gram CO_2 and 0.2293 gram H_2O.
II. 0.3370 gram gave 0.9464 gram CO_2 and 0.2423 gram H_2O.
III. 0.2286 gram gave 0.0235 gram N.
IV. 0.1792 gram gave 0.01845 gram N.

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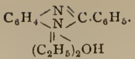
[1] This diethyl base and its salts have been formed by Simon and Pichler (cf. Annalen der Chemie **210**, 360) by heating the anhydro-base with ethyl iodide at 260°, giving the triiodide, which is decomposed by $Pb(OH)_2$ and KOH. As there were some marked differences, I used also this method of forming the base, and am led to the conclusion that the base formed from the triiodide is identical with that from the monoiodide. The former base as described melted at 132° C., was very soluble in petroleum ether; the iodide contained no water of crystallisation, and the chloride differed very materially. These seem to be errors of observation, caused by an insufficiency of material.

Calculated for



$C_6H_4<\overset{N}{\underset{N}{}}>C.C_6H_5.$ $(C_2H_5)_2OH$

	Calculated for $C_6H_4\langle N_2\rangle C.C_6H_5$, $(C_2H_5)_2OH$	Found.	
		I & III.	II & IV.
C	76.12	76.75	76.59
H	7.46	7.84	7.98
N	10.45	10.30	10.29
O	5.97		

Diethyl-anhydro-benzdiamido-benzene iodide, $C_{13}H_9N_2:(C_2H_5)_2I$, H_2O.—Crystallises rapidly out of a hot concentrated aqueous solution in fine colorless needles; if the solution is less concentrated the crystallisation is slow, and prisms, sometimes long and slender, sometimes short and thick, and pale straw color, are formed. It is easily soluble in hot water, rather difficultly in cold; the solution is very slowly decomposed by long standing, iodine being liberated; the crystals become opaque upon heating.

Analysis:

I. 0.1612 gram gave 0.0952 gram AgI.
II. 0.1581 gram gave 0.0939 gram AgI.
III. 0.2786 gram gave 0.1608 gram AgI.
IV. 0.2314 gram lost at 135° C. 0.0110 gram H_2O.
V. 0.3113 gram lost at 140° C. 0.0140 gram H_2O.

	Calculated for $C_{13}H_9N_2:(C_2H_5)_2I, H_2O$.	Found.		
		I & IV.	II & V.	III.
I	31.98	31.92	32.06	31.80
H_2O	4.55	4.75	4.50	

Diethyl-anhydro-benzdiamido-benzene chloride, $C_{13}H_9N_2:(C_2H_5)_2Cl$, $2H_2O$.—Formed by dissolving the hydroxide in hydrochloric acid, neutralising the solution with soda, evaporating to dryness, and extracting with absolute alcohol. It crystallises from a concentrated neutral solution in colorless tables, which remain unchanged in the air, and are easily soluble in water. It loses its water of crystallisation over sulphuric acid or at 100° C. The neutral solution of the chloride decomposes slowly by standing.

Analysis:

0.2694 gram lost at 100° C. 0.0301 gram H_2O and gave 0.12 gram AgCl.

	Calculated for $C_{13}H_9N_2:(C_2H_5)_2Cl, 2H_2O$.	Found.
Cl	11.01	11.01
H_2O	11.18	11.18

A second chloride crystallises imperfectly out of a very concentrated acid solution, with one molecule of hydrochloric acid and several molecules of water. By long standing over sulphuric acid or by heating, the water is given off molecule by molecule; at 130° C. the salt contains two molecules of water, which it loses below 165° C., and at the same time a molecule of hydrochloric acid is given off, leaving the anhydrous monochloride above described.

Double platinum chloride, $[C_{13}H_9N_2 : (C_2H_5)_2Cl]_2PtCl_4$.—Precipitated from a solution of the chloride by platinic chloride in very fine orange crystals; from a hot solution the crystals are sometimes quite large.

Analysis:

I. 0.1994 gram gave 0.0433 gram Pt.

II. 0.2073 gram gave 0.0446 gram Pt.

	Calculated for $[C_{13}H_9N_2 : (C_2H_5)_2Cl]_2PtCl_4$.	Found. I.	II.
Pt	21.60	21.71	21.51

Diethyl-anhydro-benzdiamido-benzene sulphate, $C_{13}H_9N_2 : (C_2H_5)_2 O.SO_2.OH, H_2O$.—Crystallises out of a concentrated aqueous solution in large flat colorless crystals. It loses its water of crystallisation very rapidly over sulphuric acid, but not over calcium chloride.

Analyses:

I. 0.1828 gram gave 0.1190 gram $BaSO_4$.

II. 0.4276 gram lost 0.02105 gram H_2O and gave 0.2720 gram $BaSO_4$.

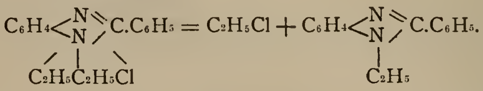
III. 0.1528 gram lost 0.0076 gram H_2O.

IV. 0.1328 gram lost 0.0065 gram H_2O.

V. 0.4707 gram lost 0.0231 gram H_2O.

Calculated for $C_{13}H_9N_2 : (C_2H_5)_2SO_4H, H_2O$.		Found. I & III.	II.	IV.	V.
H_2O	4.92	4.92	4.92	4.88	4.91
S	8.74	8.92	8.74		

Ethyl-anhydro-benzdiamido-benzene.—When the chloride is heated to a temperature above 200° C. it gradually decomposes, giving off a gas resembling in odor ethylchloride, and a thick oil distils over. This oil may be purified by dissolving in acids and reprecipitating with ammonia. It is extremely soluble in all solvents, except water and petroleum ether, being in these but slightly soluble; after the evaporation of the solvent it remains as an oil; but by gently warming, to drive away the last traces of the solvent, and then allowing it to stand several hours, it becomes gradually crystalline. Analysis proved that this compound is monoethyl-anhydro-benzdiamido-benzene. It melts at 80°–81° C. and possesses basic properties, not, however, as strong as those of the corresponding diethyl base. The reaction for the formation of this base is the following:



$$C_6H_4 < \underset{C_2H_5C_2H_5Cl}{\overset{N}{N}} > C.C_6H_5 = C_2H_5Cl + C_6H_4 < \underset{C_2H_5}{\overset{N}{N}} > C.C_6H_5.$$

This process could undoubtedly be applied to similar dialkyl anhydro-bases, as a definite method of forming the monoalkyl compounds, which have hitherto been the result of no known conditions. It is worthy of note that the salts of the monoethyl base are very unstable, being decomposed by boiling with even dilute acids, forming the corresponding salt of the anhydro-base. The corresponding salts of the diethyl base are comparatively stable, being unaffected even by strong acids, and only decomposed at quite high temperatures. The salts of the diethyl base are much more soluble in water than those of the monoethyl base; the monoethyl base, however, is itself somewhat soluble in water, while the diethyl base is insoluble. The following are analyses of the monoethyl base and its salts:

Ethyl-anhydro-benzdiamido-benzene, $C_{13}H_9N_2.C_2H_5$.

I. 0.1405 gram gave 0.4158 gram CO_2 and 0.0872 gram H_2O.
II. 0.1361 gram gave 0.0172 gram N.
III. 0.1354 gram gave 0.0170 gram N.

	Calculated.	Found.		
		I.	II.	III.
C	81.08	80.71	...	...
H	6.30	6.90	...	...
N	12.61	...	12 64	12.56

Hydrochloric acid salt, $C_{13}H_9N_2 : C_2H_5HCl, 3H_2O$.—Formed by dissolving the base in warm hydrochloric acid; crystallises in fine short colorless needles, easily soluble in water. It is decomposed by heating to slightly over 100° C.

Analysis:

I. 0.381 gram dry salt gave 0.2165 gram AgCl.
II. 0.142 gram dry salt gave 0.0786 gram AgCl.

Calculated for $C_{13}H_9N_2 : C_2H_5HCl$.		Found. I.	II.
Cl	13.73	14.04	13.69

III. 0.1683 gram air-dried salt lost at 100° C. 0.0263 gram H_2O.
IV. 1.0104 gram air-dried salt lost over H_2SO_4 in six days 0.17 gram H_2O.

Calculated for $C_{15}H_{14}N_2$: HCl, $3H_2O$.		Found. III.	IV.
H_2O	17.28	15.63	16.82

Double platinum chloride, $[C_{13}H_9N_2 : C_2H_5HCl]_2PtCl_4$.—Thrown down from a solution of the hydrochloric acid salt by platinic chloride as a very fine yellow crystalline precipitate; insoluble in petroleum ether, benzene, ether, chloroform, and but slightly soluble in hot water, alcohol, and acetone.

Analysis:

I. 0.1757 gram gave 0.0401 gram Pt.
II. 0.6994 gram gave 0.1595 gram Pt.

Calculated for $[C_{15}H_{14}N_2 : HCl]_2PtCl_4$.		Found. I.	II.
Pt	22.89	22.82	22.81

Nitric acid salt, $C_{13}H_9N_2 : C_2H_5HNO_3,H_2O$.—Formed by dissolving the base in warm dilute nitric acid, and crystallises in beautiful, fine, colorless needles, whose melting point is 155° C.

Analysis:

I. 0.319 gram lost at 100° C. 0.0188 gram H_2O.
II. 0.2709 gram melted salt gave 0.0391 N.

Calculated for $C_{13}H_9N_2 : C_2H_5HNO_3$, H_2O.		Found. I.
H_2O	5.94	5.89

Calculated for $C_{13}H_9N_2 : C_2H_5HNO_3$.		Found. II.
N	14.73	14.44

Derivatives of anhydro-benzdiamido-benzene.—The annexed table presents a comparative view of all the derivatives of anhydro-benzdiamido-benzene, and is compiled from Prof. Hübner's articles in the Annalen der Chemie, **208**, 305, and **210**, 347 ff., dissertations by Dr. C. S. Merrick (Göttingen, 1882), and Dr. F. Rinne (Göttingen, 1883), and the writer's own researches.

Dr. Merrick's work calls attention to the different hydrochloric acid salts of the anhydro-base and the peculiar double iodide of the anhydro-base and the diallyl derivative, and also the existence of two allotropic forms of the hydriodic salt of the diallyl derivative. One of these crystallises out of petroleum ether, and the other out of chloroform, though after being once crystallised, each could be recrystallised in either solvent without losing its characteristic form. That crystallised out of chloroform is unstable, and gradually becomes opaque. Both forms were measured by Dr. Rinne, and are monoclinic, the former approaching very nearly the rhombic system, and showing the forms ∞P and oP. — $\beta = 89° 35' 37''$; the latter showing oP, $\infty P \infty$, $+ P$, $- P$ and $\beta = 85° 15'$.

LABORATORY OF THE CENTRAL UNIVERSITY, RICHMOND, KY., *October*, 1883.

ON THE CONDUCT OF MOIST PHOSPHORUS AND AIR TOWARDS CARBON MONOXIDE.

BY IRA REMSEN AND E. H. KEISER.

In a paper recently published[1] we described some experiments which led us to the conclusion that when a mixture of carbon monoxide and air is brought in contact with moist phosphorus there is no oxidation of the monoxide. This conclusion is directly opposed to that reached by Leeds[2] and by Baumann,[3] according to whom the oxidation is easily effected. If these chemists are right, it follows that when moist phosphorus acts upon oxygen, something is formed which is distinct from free oxygen and from ozone. To this the name active oxygen has been given. Since our paper appeared, both Leeds[4] and Baumann[5] have published the results of new experiments, and, as we suggested that their error might be due to the action of ozone on organic substances present, such as cotton wool, rubber, corks, etc., they have carefully avoided such contact. Leeds finds no occasion to modify in the slightest degree his first statement on the subject. Baumann, however, who has taken great care in the construction of his apparatus, and whose paper gives clear indications of accurate work, obtains results which differ in some respects from those described by him in his first paper.[1] In the latter, in speaking of the passage of the mixture of air and carbon monoxide over the phosphorus, he says: "das vorgelegte Barytwasser wird schon nach kurzer Zeit trübe und im Laufe einer Stunde bildet sich ein reichlicher Niederschlag von kohlensaurem Baryt." In this experiment the gases were used in the proportion three volumes of oxygen to one of the monoxide. The whole description is such as to leave upon the mind of the reader the impression that the oxidation is very easily effected. In his last paper Baumann is much more cautious, and, though he still insists that the carbon monoxide is oxidised, the extent of the oxidation appears to have been much less than in the first experiments. Instead of getting an abundant precipitate (reichlicher Niederschlag), only a small one was obtained, and the formation of this required a much longer time, as appears from the following passage: "Nach den ersten zwei Stunden zeigte sich schon eine deutliche Trübung . . . die von da ab stetig zunahm: da der Niederschlag hauptsächlich im Innern der Zuleitungsröhre . . . abgeschieden wurde, wurde letztere nach weiteren 10 Stunden verstopft."

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[1] This Journal, **4**, 454.

[2] Journal American Chemical Society, **1**, 322.

[3] Zeitschrift für physiologische Chemie, **5**, 250.

[4] Chemical News, **48**, 25.

[5] Berichte der deutschen chemischen Gesellschaft, **16**, 2146.

Another point which arrests attention when the paper is read critically is this, that in order to get evidence of oxidation, very large volumes of air mixed with a little monoxide are passed over the phosphorus. In one case 200 cc. of the monoxide are admitted every two hours. In another the author speaks of using 700 cc. of the monoxide "in starker Verdünnung mit Luft," the passage requiring 15 hours. The amount of carbon dioxide obtained was 0.0366 gram, or 2.6 per cent. of the monoxide was oxidised. In still another experiment, a mixture consisting of 30 litres of air and 2.45 litres of the monoxide occupied 12 hours in passing the phosphorus, the amount of carbon dioxide obtained being 0.0646 gram, representing the oxidation of 1.3 per cent. of the monoxide.

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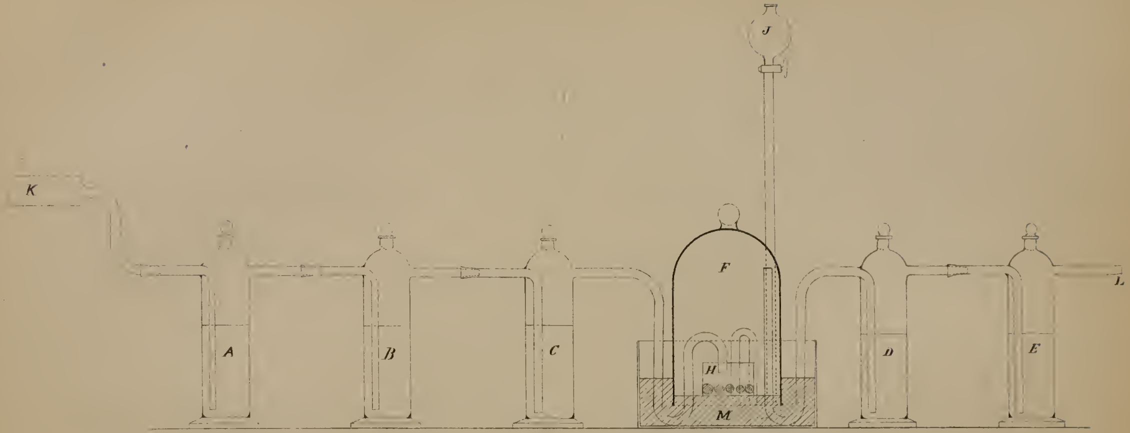
[1] *Loc. cit.*

Of course there can be no objection to using large volumes of air, provided it can be shown by blank experiments that no error is introduced in consequence, and this Baumann appears to have done. Speaking of passing air alone through the apparatus he says: "Hält man den Luftstrom so, dass . . . in der Secunde nicht mehr als zwei bis drei Blasen hindruchtreten, so entsteht . . . auch nach mehreren Tagen nicht mehr als eine ganz leichte Trübung von phosphorsaurem resp. phosphorigsaurem Baryt."

Passing now to Leeds's new experiment, but a few words will be necessary. This writer filled a glass-stoppered 10-litre flask with a mixture of equal parts of carbon monoxide and air, and allowed the mixture to stand in contact with moist phosphorus for six days. Then the glass stopper was removed, replaced by a cork, and, the mouth of the vessel being placed under mercury, the gases were displaced and passed through baryta water. A precipitate representing 0.0155 gram of carbon dioxide was obtained. There is one source of error in this experiment which should be noted at once. It is clear that by standing for six days in the tightly closed vessel, the oxygen of the air must have been completely used up, so that the gases were necessarily under diminished pressure. Apparently, in taking out the glass stopper for the purpose of introducing the cork, no precautions were taken to prevent access of ordinary air, and a considerable volume of ordinary air must have entered; not enough certainly to give the quantity of carbon dioxide obtained, but enough to cause a perceptible precipitate in the baryta water. Another source of error, however, much more serious than this, and quite sufficient to account for the result, has since been discovered by us.

Although we felt convinced of the accuracy of our first work and the correctness of the result, we have nevertheless subjected the work to a careful revision. Working with the precautions previously used, we have obtained exactly the same results as at first. On studying Baumann's paper, however, it seemed to us possible that there might be a slight oxidation, so slight as to escape notice when comparatively small volumes of the gases are used. Now, in most of our first experiments small volumes were used, and we therefore felt it incumbent upon us to go over the work, using larger volumes. We first passed thoroughly purified air through an apparatus which was so arranged as to prevent all contact of ozone with organic substances. The current was fully as slow as that in


J
K
F
L
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C
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D
E
M

Baumann's experiments, and the gases, after passing out of the ozonising vessel, were washed with a rather larger quantity of water than was used by Baumann. A cloudiness began to appear in the baryta water after six or eight litres of air had passed through, and this increased constantly, until when 25 to 30 litres had passed in 12 to 15 hours a distinct precipitate, not a mere turbidity, was in the vessel containing the baryta water. The precipitate was carefully examined with reference to the presence of phosphorus compounds, but not a trace could be detected. The experiment was repeated with the same result. It is clear, therefore, that in spite of Baumann's explicit statement, there is some source of carbon dioxide independent of carbon monoxide, and before accurate experiments can be made this source must be discovered and if possible avoided.

Karsten[1] has shown that when air alone comes in contact with the organic matter of corks and connectors, carbon dioxide is formed, and that if a large volume of air is first freed from carbon dioxide and then passed through lime water, a precipitate is formed, unless all contact with organic matter is prevented. Storer[2] has recently confirmed this observation. It hence seemed possible that the carbon dioxide obtained from the air in our experiment might be formed either from the organic matter in the air or by the action of the air on the rubber connectors and corks of the wash bottles used in purifying it, and our next step was to so arrange our apparatus as to absolutely exclude all organic matter. This was effected by means of an apparatus illustrated in outline in the figure. The wash bottles *A*, *B*, *C*, *D*, *E*, were made for us by a skillful glassblower. They are fitted with glass stoppers, and the escape tube of each fits air-tight into the entering tube of the next one by means of a ground glass joint. The tube, *K*, only partly represented in the figure, is about 14 inches long and of hard glass. The vessel, *F*, is an ordinary bell jar, holding about one and a quarter litres. This is held in position on mercury contained in a crystallising dish. Upon the mercury floats a smaller vessel, in which the phosphorus is placed. The tube from the last wash bottle through which the air is passed before it comes in contact with the phosphorus is bent so as to pass beneath the edge of the bell jar, then up into the closed space above the mercury, and then down towards the phosphorus. The tube through which the carbon monoxide is passed into the vessel is arranged in the same way. A long funnel tube, *J*, is bent in a similar way, but reaches down to the bottom of the dish containing the phosphorus. By means of it the phosphorus can be covered with water or uncovered, as may be desired, without disarranging the apparatus. The tube through which the gases pass out of the bell jar is bent like the two already referred to, with the exception that it is not directed downward after entering the vessel, but is allowed to project nearly to the top of the space. All joints which are not of ground glass are carefully fitted by means of gypsum.

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[1] Poggendorff's Annalen, **115**, 348.

[2] This Journal, **5**, 69.

This is the apparatus exactly as it was used in a number of experiments with air alone. The method of experimenting was as follows: The air was contained in a gasometer holding 30 litres. From this it was passed slowly, at the rate of about two or three bubbles per second, into the hard glass tube, *K*, containing copper oxide heated to dull redness; then through the three wash bottles, the first two containing caustic soda, and the last one baryta water. It was then passed into the bell jar containing the phosphorus. Care was taken to keep the air in this vessel as near 24° as possible, and the white fumes indicating the action of the phosphorus were always abundant during the course of an experiment. The amount of phosphorus exposed, that is, not covered by water, varied from 20 to perhaps 70 or 80 grams, the usual amount being between 20 and 30 grams. From the bell jar the ozonised air with whatever it contained passed through the wash bottle, *D*, containing from 30 to 40 cc. of pure distilled water, and then into the concentrated baryta water. The last bottle, *E*, containing the baryta water was connected with a tube containing caustic potash to protect it from the ordinary air.

We cannot see how any exception can be taken to the apparatus used by us, or to the method of conducting the experiments. Nevertheless, working under what appear to us to be perfect conditions, we obtained exactly the same result as we had obtained in the first experiments with air, viz. the air alone when passed for a sufficient length of time gave a precipitate in the last bottle. Ten litres of air always cause a distinct turbidity, and twenty to thirty give a precipitate. As there was no possible source of error, it follows that the carbon dioxide obtained must have come from carbon contained in the phosphorus. There is no escape from this conclusion. That there should be carbon in phosphorus is not surprising when we consider the method of manufacture and the fact that boron, silicon, iron, etc., which are made by similar methods, all contain small quantities of this element. Indeed, the presence of carbon in the phosphorus as it is at first obtained is well known, and, in the purification process adopted, chromic acid is used for the purpose of removing it. *A priori* we would hardly expect the process of purification to be complete, and our experiments furnish the proof that it is not.

Whether the carbon is present in the phosphorus in chemical combination or not is a question difficult to answer. We can only say that the phosphorus used by us appeared to be perfectly homogeneous. There was no evidence of the presence of particles in it. Its solution in carbon bisulphide was clear, and on standing nothing whatever was deposited. Some of the phosphorus which we used had been carefully redistilled by us. This made no difference in the result. These facts lead us to believe that the carbon is in chemical combination with the phosphorus.

We have made some attempts to estimate the quantity of carbon present, but have not been successful. A simple way to show its presence is to burn a piece of phosphorus in a small porcelain dish floating on water under a bell jar fitted with a glass stopcock. After the combustion is over, the vessel is allowed to stand for some time until the white fumes have entirely disappeared. The gas is then passed through water and finally into baryta water, where a not insignificant precipitate is invariably formed. The air in the bell jar must, of course, be purified. As the vessel is lifted only far enough to permit the introduction of the dish with the phosphorus, and this operation is performed instantaneously, the amount of carbon dioxide introduced with the air can be only infinitesimal.

The complete oxidation by means of chromic acid of a weighed quantity of phosphorus, and estimation of the carbon dioxide formed, gave unsatisfactory results, for the reason that it was impossible to regulate the action and at the same time secure complete oxidation of the phosphorus. With concentrated solutions the action is liable to become very violent unless the temperature is kept low. By means of the experiments with chromic acid we were able to demonstrate the presence of the carbon by the formation of a precipitate of barium carbonate, but though the precipitate was weighed in a few cases, the results are of little value, as the action was evidently incomplete.

Similar experiments with nitric acid were equally unsuccessful as quantitative analyses, though they also clearly showed the presence of carbon.

Finally an apparatus was arranged similar to that used for making phosphorus pentoxide on the small scale. The combustion was effected in pure air, and after being thoroughly washed the gases were passed through baryta water. Again a precipitate was formed, but the operation was far from perfect, owing to the formation of a considerable quantity of red phosphorus, and to imperfect oxidation.

For the present we have given up the attempt to estimate the quantity of carbon in phosphorus, and content ourselves with having proved beyond question that it is present in sufficient quantity to interfere with such delicate experiments as those upon the oxidation of carbon monoxide.

We now made some experiments with the object of determining how far changes in the amount of phosphorus exposed in the ozoniser perceptibly changed the amount of barium carbonate formed. We found that the amount of the precipitate is plainly influenced by the rate of passage of the gases, the temperature, and the amount of phosphorus exposed, but that, if the temperature is between 20 and 25°, the rate of passage of the air about two or three bubbles per second, and the amount of phosphorus exposed from 20 to 30 grams, a slight precipitate is always formed by 10 litres of air, and that 25 to 30 litres give a very decided precipitate.

It does not of course follow from the facts above described that carbon monoxide is not oxidised by air in the presence of moist phosphorus, but it is clear that in experiments undertaken for the purpose of deciding the question, allowance must be made for the presence of carbon in the phosphorus. The amount of allowance to be made cannot be determined with accuracy, for the amount of phosphorus exposed cannot be perfectly controlled in the apparatus used. The best way to reach a positive conclusion is to perform parallel experiments under as nearly the same conditions as possible, one with air alone, the other with air and carbon monoxide. If the vessels in which the precipitates are formed are of the same shape and size and each contains the same amount of baryta water, we can judge with a fair degree of accuracy whether a larger precipitate is formed in one case than the other.

In making these comparisons about 25 litres of air were first passed through the apparatus, the conditions being carefully noted. The bottle containing the precipitate formed was removed at the end of the operation, instantly stoppered and placed aside for comparison. The water was then removed from the wash bottle, and replaced by fresh distilled water, a new bottle attached in the place of *E*, and after passing about a litre of pure air through the apparatus, the necessary quantity of baryta water filtered rapidly through a plaited filter into the wash bottle. Now the experiment was repeated with the difference that during the passage of the 25 litres of air, a very slow current of carefully purified carbon monoxide (made from pure sulphuric and formic acids) was passed through three wash bottles like those used for the air and containing the same substances, and then, through the tube described above, brought into the presence of the phosphorus and air. The rate of the current was so regulated that, during the time of the experiment, which varied in different cases from three to eight hours, three litres of the monoxide were used. The same slow formation of a precipitate was noticed when the carbon monoxide was used as in the case of air alone. At the end of the operation we were unable to distinguish any difference between the amounts of the small precipitates formed. In neither case did this amount appear to be as great as that found by Baumann. The precipitates were too small to permit of accurate filtering and weighing, if we consider the nature of the liquid in which they were present. Comparing their size with that of certain larger precipitates which we did weigh, we estimated that they could not possibly weigh more than one to two milligrams. If there was any difference between them it could not have amounted to more than a small percentage of the total weight, and, as already said, no difference was apparent. The only conclusion which we can draw is, as we claimed in our first publication on this subject, that carbon monoxide is not oxidised by air in the presence of moist phosphorus.

The precipitate obtained by Leeds, which he ascribed to oxidation of the carbon monoxide, must have been due mainly to the oxidation of the carbon in the phosphorus. We have shown that the amount of carbon dioxide formed by burning phosphorus in a few litres of pure air is considerable; quite enough, we should judge, to give a precipitate as large as that obtained by Leeds.

The fact that Baumann obtained precipitates when working with large volumes of air is easily understood; but that they should have been as large as they were is not easily explained. That only a slight turbidity should have been obtained after several days, on passing air alone through the apparatus, is beyond our comprehension.

That in our first experiment we should have obtained no evidence of the presence of carbon is due to the fact that we worked with small volumes of the gases. In those cases in which relatively large volumes were used the slight cloudiness produced was disregarded, as the same result was obtained with air alone. We are further inclined to think that the moist asbestos through which the gases were passed may have retained a small quantity of the carbon dioxide. We have found that this method of filtering is quite superfluous, and that the water in the small wash bottle is sufficient to retain all traces of phosphorus compounds. Phosphorus could never be detected in the precipitate of barium carbonate, and, indeed, when the current was as slow as usual, phosphorus compounds were not found in the first wash bottle.

Although our experiments have cost us a great deal of time and labor, the apparatus finally used is simple and the experiments may be repeated with comparatively little trouble. We therefore hope that others who may be interested in the subject may find the time to repeat them. It is, however, absolutely necessary that all the precautions mentioned by us be taken.

It certainly appears remarkable that carbon monoxide is not oxidised by air in the presence of moist phosphorus where the formation of ozone is constantly taking place. If our ordinary conceptions in regard to this process are correct, the phosphorus splits up the molecules of oxygen and unites with some of the atoms thus set free, while other oxygen atoms rearrange themselves in the form of ozone molecules. There should, according to this conception, be free atoms of oxygen in the immediate vicinity of the phosphorus, and the first thought would naturally be that an unsaturated compound like carbon monoxide must be oxidised. That it is not is, however, quite in accordance with its conduct towards ozone during the transformation of the latter into ordinary oxygen. One of us (R.) has shown[1] that, if carbon monoxide be mixed with ozone, and the mixture passed through a tube heated to about 300°, a temperature sufficiently high to transform all the ozone into oxygen, no oxidation of the monoxide takes place. In this experiment we have conditions exactly the opposite of those involved in the phosphorus experiment. In both cases, however, according to the prevailing notions, free atoms of oxygen ought to be formed and to exist in the interval, however brief it may be, between the breaking up of the ozone and the formation of oxygen or the splitting up of the molecules of oxygen and the formation of ozone.

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[1] This Journal, **4**, 50.

Why carbon monoxide is not oxidised by ozone itself under ordinary circumstances is a question which it is impossible to answer in the present state of our knowledge; still less can we imagine a reason for the fact that it is not oxidised by the gases formed when ozone is broken up by heat, nor by those formed during the production of ozone by the action of phosphorus on moist air.

There is at present then only one experiment on record which seems to show that by starting with ordinary oxygen this can be so changed as to acquire the power to oxidise carbon monoxide at lower temperatures. This is the experiment of Baumann[1] with palladium hydrogen. In view of the fact that Traube has shown[2] that palladium and hydrogen dioxide together can readily oxidise the monoxide, an observation which we have confirmed,[3] and that hydrogen dioxide is formed, though apparently in small quantity, by the action of palladium hydrogen on air and water, the question as to the cause of the oxidising action of palladium hydrogen may fairly be regarded as an open one.

The observation of Leeds that when a mixture of carbon monoxide and air is submitted to the silent electrical discharge carbon dioxide is formed, furnishes no evidence of the formation of active oxygen, as Andrews and Tait[4] have called attention to the fact that when the silent discharge acts upon carbon monoxide alone some dioxide is formed.

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[1] Zeitschrift für physiologische Chemie, **5**, 250.

[2] Berichte der deutschen chemischen Gesellschaft, **15**, 2854.

[3] This Journal, **4**, 454.

[4] Philosophical Transactions, 1860, p. 126.

ON THE CONSTITUTION OF RESOCYANIN.

By Arthur Michael.

About fourteen months ago I made the observation that a mixture of acetylacetic ether and resorcin heated with zinc chloride formed a new compound. A careful search in the literature of resorcin and acetylacetic ether failed to show that the reaction had been previously noticed, and I therefore made it the subject of an investigation. In a paper read a year ago before the Harvard Chemical Society, I described the compound and a number of its derivatives, and also a similar compound obtained from pyrogallol. Shortly afterwards the September number of the "Journal für praktische Chemie" was received, and in it I found a paper by M. Wittenberg[1] on the same subject, and also learnt that the reaction was discovered by W. Schmid[2] almost a year previous. W. Schmid's paper was entitled "On a new formation of Resocyanin," and the fact that I had not suspected the identity of the product from acetylacetic ether with resocyanin occasioned the oversight of his short note. Indeed, I had deduced from my work quite a different formula for the compound than that which Wittenberg and Schmid have assigned to resocyanin. I did not feel entitled, however, to publish my results, as Wittenberg evidently intended to continue his investigation. The last September number of the "Berichte der deutschen chemischen Gesellschaft" contains a paper by H. von Pechmann and C. Duisberg entitled, "On the compounds of Phenols with Acetylacetic Ether," in which these chemists describe resocyanin as a new compound under the name of β-methylumbelliferon, and are quite unaware of the previous researches of Schmid and Wittenberg. v. Pechmann and Duisberg come to the same conclusion regarding the symbol of resocyanin that I had a year previous, and I have thought that under these circumstances the analytical results I obtained might be published without it being considered an intrusion into Wittenberg's field.

My product was obtained by heating equal weights of acetylacetic ether, resorcin and zinc chloride until the evolution of a gas was noticed, when the reaction proceeded without further heating.

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[1] Journal für prakt. Chemie [2], **26**, 66.

[2] *Ibid.* [2], **25**, 81.

After the effervescence ceased the mixture was heated for 15 minutes, and then poured in cold water. The crystalline product is best purified by dissolving in hot alcohol, filtering, treating with bone black, and several crystallisations from alcohol. Schmid found carbon dioxide as the only gas given off in the reaction. I think that besides this gas a small amount of ethylene is evolved; at least a gas which is not absorbed by lime water, and is by bromine.

I. 0.2626 gram of substance, dried at 110°, gave 0.6545 gram of CO_2 and 0.1131 gram of H_2O.

II. 0.2536 gram of substance, dried at 110°, gave 0.6266 gram of CO_2 and 0.1121 gram of H_2O.

III. 0.2213 gram of substance, dried at 110°, gave 0.5535 gram of CO_2 and 0.954 gram of H_2O.

	Theory for $C_{10}H_8O_3$.	Found. I.	II.	III.
C	68.18	67.98	68.35	68.21
H	4.54	4.78	4.98	4.78

For comparison the results of Schmid's, Wittenberg's and v. Pechmann and Duisberg's analyses are stated:

	v. Pechmann and Duisberg.		Schmid.	Wittenberg.		Theory for $C_{21}H_{18}O_6$.
C	68.14	68.3	68.62	68.65	68.67	68.85
H	4.7	4.7	4.96	4.94	4.92	4.91

It will be noticed that while v. Pechmann and Duisberg's, and my own analyses, agree well with the formula $C_{10}H_8O_3$, those of Schmid and Wittenberg agree better with the formula of resocyanin assigned by these chemists.

The only properties of resocyanin noticed which have not been already mentioned were, that the white powdered substance is fluorescent—this is particularly noticeable when it is enclosed between two watch-glasses; and that an alcoholic solution of the substance, allowed to cool in a very quiet place, solidified to long, white needles, occupying the whole vessel, which, when rubbed, or even if the vessel is shaken, were rapidly changed into the prismatic form, not occupying one-fifth of the space taken up by the other modification.

Acetyl resocyanin was prepared by the action of acetic anhydride and fused sodium acetate on resocyanin. It remained unchanged when heated with acetic anhydride in a closed tube. My observations on this compound agree closely with those of Wittenberg.

0.2296 gram of substance gave 0.5594 gram of CO_2 and 0.1013 gram of H_2O.

	Theory for $C_{10}H_7O_3(C_2H_3O)$.	Found.
C	66.05	66.46
H	4.58	4.90

To obtain the methyl derivative of resocyanin, that compound was dissolved in methyl alcohol containing methylsodium oxide, and an excess of methyl iodide added. After standing 12 hours, white needles separated from the clear solution, and the reaction was completed by heating for one-half hour at 100°, when the solution solidified on cooling. The substance was treated with cold dilute sodium hydrate, and the insoluble residue purified by crystallisation from hot alcohol.

0.2165 gram of substance gave 0.5496 gram of CO_2 and 0.1068 gram of H_2O.

	Theory for $C_{10}H_7O_3(CH_3)$.	Found.
C	69.46	69.25
H	5.26	5.48

This substance crystallises from hot alcohol on cooling in long white needles, melting at 158°–159°. The substance is insoluble in cold alkalies, but on warming a solution is effected, from which the addition of an acid precipitates the original substance. According to v. Pechmann and Duisberg, the methyl derivative, on boiling with alkalies, takes up water, passing over into the salt of an acid.

Resocyanin treated with nascent hydrogen takes up hydrogen. For this purpose it was dissolved in aqueous sodium hydrate, and treated with sodium amalgam until a drop of the reduced liquid poured into water failed to cause the characteristic blue fluorescence of resocyanin. The addition of acids to the alkaline solution gave a half-solid white precipitate, which soon solidified. For purification it was crystallised several times from dilute alcohol.

0.1970 gram of substance, dried at 110°, gave 0.4902 gram of CO_2 and 0.0971 gram of H_2O.

0.2425 gram of substance, dried at 110°, gave 0.6057 gram of CO_2 and 0.1170 gram of H_2O.

	Theory for		Found.	
	$C_{10}H_{10}O_3$.	$C_{10}H_9O_3$.		
C	67.41	67.80	67.82	68.16
H	5.61	5.08	5.42	5.36

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[illegible]				[illegible]	[illegible]	[illegible] Melting point [illegible] needles, [illegible] plates, [illegible] acetic acid.	[illegible] Melting point [illegible] crystals [illegible] acetic acid [illegible] and benzene.
[illegible]		[illegible]	[illegible] Long needles [illegible]	[illegible] H_2O.	[illegible] H_2O Large [illegible] easily sol. [illegible]	Picrate. $C_{13}H_9N_2 \cdot C_6H_2(OH)(NO_2)_3$ Melting point 116° C. Small yellow [illegible] H_2O and alcohol.	
[illegible] HNO_3 Fine needles [illegible] H_2O	[illegible] HNO_3 [illegible] Melting point [illegible] [illegible] sol. in H_2O	[illegible] Melting point [illegible]		[illegible] easily [illegible] H_2O	[illegible]		$C_{13}H_9N_2$ [illegible] Melting point [illegible] needles, [illegible]

This reduction product is insoluble in hot water, soluble in hot dilute alcohol, and separates on cooling as slender prisms with straight end-faces. In order to obtain the correct melting point it is necessary to heat a paraffin bath almost to the melting point of the substance—about 255°—as prolonged heating below its melting point causes it to blacken before melting. The melting point obtained in this manner was 257°–259°. Dilute alkalies dissolve the substance in the cold, and the addition of an acid precipitates the original substance. The alkaline solution does not show any fluorescence, but became slightly fluorescent on standing exposed to the air. This indicates that resocyanin was re-formed by oxidation.

The reduced substance is converted by the action of acetic anhydride and sodium acetate into an acetyl derivative. The product of the reaction was extracted with water, and the insoluble residue crystallised several times from alcohol.

0.2325 gram of substance, dried at 110°, gave 0.5625 gram of CO_2 and 0.1126 gram of H_2O.

	Theory for		Found.
	$C_{10}H_9O_3(OCCH_3)$.	$C_{10}H_8O_3(OCCH_3)$.	
C	65.45	65.75	65.98
H	5.45	5.02	5.38

This compound crystallises from alcohol as colorless, glittering, rhombic prisms with macrodiagonal domes, and melts at 221°–222°. It is insoluble in boiling water, sparingly soluble in hot dilute alcohol, moderately in hot alcohol. In boiling glacial acetic acid it is more soluble than in hot alcohol. The results of the analyses of hydroresocyanin are better in accordance with the formula $C_{10}H_9O_3$ than with $C_{10}H_{10}O_3$. Although I do not consider the analytical data as settling conclusively the symbol of hydroresocyanin, it appears probable from them that the symbol of resocyanin should be doubled, $C_{20}H_{16}O_6$ instead of $C_{10}H_8O_3$, as the addition of a single atom of hydrogen could hardly result other than from the reduction of carbonyl and the formation of a pinacone. This, however, would give hydroresocyanin four hydroxyls, whereas the analysis of the acetyl product showed that the compound contains but two hydroxyls.

Wittenberg obtained resorcin from resocyanin by fluxing with potassium hydrate. My observations agree with those of v. Pechmann and Duisberg, that boiling with concentrated alkali decomposes the substance, forming resorcin almost quantitatively. The decomposition is dependent on the concentration of the alkaline solution; and, as would seem from several experiments, also on the relative amount of alkali. Resocyanin may be boiled for several days with dilute caustic potash without undergoing decomposition. My experiments on the relation between the decomposition and quantity of alkali are very meagre, and are only several preliminary observations which I had made several days before the knowledge of Wittenberg's research caused me to discontinue my work. I found that a concentrated solution of resocyanin in potassium hydrate, in the proportion of one molecule of the former to two of the latter compound, required continued heating before a noticeable decomposition ensued, while, when these substances were taken in the proportion of one to three molecules, the resocyanin was decomposed in a few hours. What appears more striking is the observation that with the further addition of alkali the decomposition became much slower; when the compounds were taken in the proportion of one to four molecules the resocyanin was not entirely decomposed after heating for ten hours. This subject certainly merits further investigation.

Bromine[1] added in excess to resocyanin, dissolved in acetic acid, gave a precipitate which is very slightly soluble in alcohol, somewhat more soluble in hot glacial acetic acid. It crystallises in small rhombohedric crystals, melting at 240° (Wittenberg's compound melted at 250° and contained 57.14 per cent. Br.)

	Theory for $C_{10}H_5Br_3O_3$.	Found.	
Br	58.11	57.54	58.28

Bromine has no action on this compound in the cold; the substance, when allowed to stand with bromine dissolved in carbon disulphide and exposed to the sunlight for several days, was regained on evaporation of the bromine. Two grams of the tribrom compound heated with one gram of potassium hydrate dissolved in 25 cc. of water, formed a yellow solution which soon turned green. The addition of chlorhydric acid to the green solution gave a purple precipitate which, crystallised from dilute alcohol, formed clusters of white needles melting at 192°–195°.

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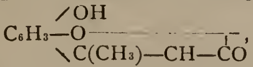
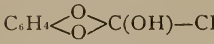
[1] The following observations and analyses were made by my former assistant, Mr. A. M. Comey.

Resocyanin is completely oxidised in the cold, by potassium permanganate, to carbonic acid. A gram of the substance was dissolved in caustic potash, and one gram of the permanganate dissolved in water, added to the cold solution. The filtrate contained resocyanin; this was also found to be the case after addition of a second gram of permanganate. The further addition of ½ gram permanganate was sufficient to effect complete oxidation, as the solution then contained only potassium carbonate.

Equal weights of resocyanin and zinc chloride melted together form a red flux. This treated with water gave a crystalline substance, which was probably a zinc derivative of resocyanin, since it contained that metal, and when treated with chlorhydric acid gave resocyanin.

Another reaction, which was not further examined, is the action of phosphorus pentachloride dissolved in phosphorus oxychloride on resocyanin. On heating, the mass took a dark violet color, and from the filtrate obtained by pouring it into water and filtering while warm, red crystals separated, which melted between 97°–102°. These crystals boiled with water for some time gave crystals melting at 180°, which were probably not quite pure resocyanin.

It may not be amiss to make a few remarks on the theoretical considerations regarding the constitution of resocyanin that are found in Wittenberg's and v. Pechmann and Duisberg's papers. The first-named chemist has devoted several pages to the discussion of an extremely complicated structural formula, which is based solely on the analyses of the substance and its acetyl derivative. That these analyses are slightly wrong is probable from v. Pechmann and Duisberg's work, and also from the results mentioned in this note; but, at all events, v. Pechmann and Duisberg's results on the methyl derivatives, and the behavior of resocyanin towards nascent hydrogen, show the impossibility of the structural formula proposed by Wittenberg. v. Pechmann and Duisberg have suggested a more probable constitution for resocyanin,  $C_6H_3\begin{array}{l}\diagup OH\\ -O-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!\rceil\\ \diagdown C(CH_3)-CH-CO\end{array}$, but the following points need elucidation before it can be accepted: Firstly, absolute certainty in regard to the symbol of resocyanin; secondly, the properties of resacetophenon, as I have previously stated,[1] do not agree with the constitution given by Nencki, $\overset{(OH)_2}{C_6H_3}CO{-}CH_3$, but better with  $C_6H_4{<}\substack{O\\O}{>}C(OH){-}CH_3$; thirdly, the results obtained by reduction indicate that resocyanin goes over into a substance with one atom more hydrogen, whereas umbelliferon on reduction adds two atoms of hydrogen and a molecule of water; and finally, absolute proof of the identity of the product obtained by oxidation of the dimethyl derivative with β-dimethylresorcylic acid.

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[1] This Journal, 5, 94.

TUFTS COLLEGE, MASS., *Nov. 19th*, 1883.

MEMORANDA OF METHODS EMPLOYED BY FISHERMEN FOR "BARKING" AND IN OTHER WAYS PRESERVING NETS AND SAILS.

BY F. H. STORER.

Seafarers are familiar with the fact that upon several foggy coasts, notably those of Scotland and of the islands north of it, as well as the coasts of Cornwall, Nova Scotia, New Brunswick, and Newfoundland, the fishermen habitually tan or "bark," as the saying is, the sails of their boats, and their nets also, in order to protect them from rot and mildew. That is to say, they are accustomed to stain the sails a dingy reddish brown color by means of materials containing tannin, such as are employed in the ordinary process of tanning leather.

The process is manifestly an old one, and references to it may be found very early in the works relating to technology. But the methods employed seem to be to the last degree empirical in most localities, and the subject appears never to have received proper attention either from professional dyers or from scientific men. It is regrettable that the systematic works on dyeing, occupied as they have been with the practical and aesthetic side of the art, have hitherto paid little heed to the rough domestic processes which are of special historic interest. It is high time that these rough and often imperfect processes should be recorded and studied, both from the scientific and the archaeological points of view.

In seeking for what I might find printed concerning the tanning of sails I have come across several items which seem to be worthy of publication, as bearing upon the early history of the art of dyeing. I am the more especially impelled to print these notes, since no chemist, in so far as I am aware, has ever seriously considered the methods of coloring that are employed by the fishermen. Indeed, these processes have seldom been alluded to by chemists of late years. The common notion of deep-water sailors that the canvas to be stained is simply soaked in tan-pits, as hides are in the process of making leather, seems at first sight hardly probable in view of the depth of the color imparted to the sails in some localities, and of the well-known difficulty of dyeing strong, fast colors upon either linen or cotton except with the aid of mordants. Nevertheless, it appears that the sailors are very nearly right in their supposition, and that simple dipping of the sails in this sense, or, rather, boiling them in tan liquor, is a very general practice. Most of the references which I have found in books relate to it. Thus, in Wm. Lewis's "Philosophical Commerce of the Arts," London, 1763, 2, 429, it is stated that fishing nets receive a pretty durable stain from soaking in astringents. Chomel's "Dictionnaire œconomique," Paris, 1767, 2, 88, directs that nets may be colored by boiling them in tan liquor, or in a decoction of the bark of walnut roots; or the net may be rubbed with celandine or young wheat when a yellow or green color is wanted. So too, in Chambers's Cyclopædia, Dublin, 1782, Vol. 3, article Net (in Fowling). Similar directions will be found in several of the earlier dictionaries of rural affairs, and in many old books relating to country sports, such as hunting and fishing. In the "Dictionnaire de Marine," by Willaumez, Paris, 1825, p. 547, it is said that French fishermen soak their sails in a decoction of oak bark and red ochre to preserve them. James Anderson, in his "Account of the Hebrides and West Coast of Scotland," Edinburgh, 1785, pp. 336, 344, says that nets and sails are there tanned by simply soaking them in hot tan liquor from oak bark. The Encyclopædia Britannica, article Net, p. 105 of the edition of 1842, says the most usual color given to nets is the russet, which is obtained by plunging the net into a tanner's pit and letting it lie there till it be sufficiently tinged. This is of a double service to the net, since it preserves the thread as well as alters the color. Good, in Dingler's Polytechnisches Journal, 1820, 2, 162, explains how he tans nets and sails by boiling them in tan liquor; and the same account is given in C. Mackenzie's "One Thousand Experiments in Chemistry," London, 1821, p. 508. Millett, Polytechnisches Centrallblatt, 1847, p. 1285, cited in Elsner's Mittheilungen, 1, 124, says fishermen merely soak their nets in hot tan liquor. He himself put some linen thus treated in a damp cellar and kept it for years. Wimmer, Dingler's Polytechnisches Journal, 121, 372, repeated Millett's experiment with success. H. de la Blanchère, in his "Nouveau Dictionnaire général des Pèches," Paris, 1868, p. 763, says nets are tanned to hinder them from rotting. A quantity of ground oak bark is boiled for a couple of hours in rain water, and the still boiling liquor is poured upon the dry clean net, which has been placed in a tub. The net is well kneaded in the liquor and turned several times during the day. It is then left to soak during thirty-six or forty hours; finally it is withdrawn from the liquor and dried. The operation is repeated once a year. It has become more and more common to use catechu for tanning sea nets, and to-day most of them are preserved with this material. Being much richer in tannin than oak bark, it tans the nets more strongly and preserves them better. The operation is performed in the same way by means of hot water saturated with catechu, often admixed with oak bark to lower the price a little. The tanning of lines, also, especially for sea fishing, is an important operation, both because they last longer and because they are less visible. A dead-leaf color is obtained by chopping walnut bark or oak bark fine and boiling the fragments one hour in water. The lines are placed in the vessel among the bark and left to soak twenty-four hours. They are then taken out, wrung and dried. Catechu may be substituted for the bark; it acts quicker and gives a more solid color. A dirty orange color is obtained by collecting a quantity of the plant *Chelidonium Majus* in the fields and simply rubbing the lines with the green plant, so that they may be impregnated with the juice. The lines are then dried and the process is complete. A green color is obtained from young wheat plants chopped and pounded and boiled. The lines are soaked in the liquor twenty-four hours. In addition to the foregoing, Walton is credited by de la

Blanchère with a method of dyeing lines with walnut leaves, beer and alum.

I have myself made numerous enquiries of people likely to know something about the subject, and I am greatly obliged to many persons for the information they have given me and the pains they have taken to procure information. The well-known ichthyologist, Captain Nath. E. Atwood, of Provincetown, in particular, put me in personal communication with fishermen from Nova Scotia, who in their own country had been accustomed from early youth to the barking of nets and sails. The accounts given by these men were explicit and concordant, to the effect that the bark of fir and spruce trees was collected in the woods and boiled thoroughly in water. The nets having been placed in tubs, the tan liquor was poured over them, the bark being thrown on top, and the nets were left to soak in the liquor during twenty-four hours. This operation was usually performed once a week, the common plan being to put the nets in soak Saturday night and leave them soaking over Sunday. These Nova Scotians were emphatic that nothing whatsoever was mixed with the tan liquor, or put upon the sails in conjunction with the tan. On the contrary, it was customary, they said, to use new sails in the boats for a short time before coloring them, in order that any grease or starch in or upon the sails might be washed out by rains and worked out by use. So, too, the small amount of oily matter which is habitually put upon flax to make the fibres work more easily in the process of manufacturing it into cloth is always washed out with soap and water before the twine or canvas comes to be subjected to the tanning process. They state that when the nets are in use the color soon washes out of them, and that the process has to be frequently repeated on this account. In their eyes, the purpose of the tan liquor seemed to be rather to "kill the slime" which is left upon the nets when fish are captured, than to permanently protect the twine from putrefactive influences. They said the same process was used for sails as for nets, only the sails were not soaked so often; they were dried after soaking. Immediately after dipping the sails were very dark, but the color gradually washed out of them. Nothing was ever added to fix the color, or, as one of my informants put it, "to set the tan." This same man stated that in the domestic economy of his locality the dyeing of linen articles was habitually practised, and that his people were accustomed to use copperas and alum to set a variety of colors on household goods.

It may here be said that the use of copperas for dyeing fast blacks and browns, of various shades, as well as drabs and slate color, on cotton and linen, by means of decoctions of different barks, husks and leaves (such as those of the walnut, oak, maple, alder, beech, sumach, willow, pine, etc.), is common in American households from Nova Scotia to Florida. As I am assured by several friends, and as has frequently been published (compare, for example, Dr. F. R. Porcher's "Resources of the Southern Fields and Forests," Charleston, 1869, pp. 215-217), the traditional "butternut" garments accredited to the Southern soldiers during the war are said to have been dyed in this way. Porcher (p. 215) says, "Those who cannot obtain copperas use the water from one of the mineral springs, which is strongly impregnated with iron." On pp. 217 and 241 he urges that "vinegar and rusty iron will often fix colors without the aid of copperas"; and again, on p. 302, he says that "blacksmith's dust may be used in place of copperas." Others have suggested that, in default of copperas, the mere act of boiling the cotton and the dye-stuff in an iron pot, "preferably a clean one" (*i. e.* new and free from grease?), may help to fix the color; and it is not impossible that the influence of iron dissolved from the pot by acids in the dye-stuff may have been felt to a certain extent, in this sense, in some cases, to be alluded to directly, where fast colors are said to have been obtained by means of barks without using any mordant. Besides copperas, alum and blue vitriol are freely used in this country for various purposes in domestic dyeing,

Of late years catechu seems to have superseded bark in many localities. It is now freely used by fishermen both in Europe and America. I have myself known of boatmen occasionally soaking their mooring painters in a solution of it, to preserve them from decay, and I have seen simple catechu applied to the sails of boats, also, to preserve them from mildew. It was thought to serve a good purpose, though, unless pains are taken to turn the sail frequently while it is drying, *i. e.* while the catechu is undergoing oxidation, one side of the sail will be darker than the other.

J. G. Nall[1] says herring nets are usually made of a strong two-thread hempen twine, which undergoes a process of tanning in cutch, *i. e.* catechu, a solution of which gives the twine a brown hue. In the autumn the surface of the Yarmouth Denes, covered over with nets spread out to dry, has the appearance of a tan-pit. Oak and ash bark were formerly employed. Care has to be taken not to over-tan the nets, the meshes of which would become contracted and too much hardened. The nets are tanned in the beginning to preserve them from rotting, and the process is repeated at the close of the fishery in order to cleanse them thoroughly. A mackerel net will outlast several herring nets. They are neither exposed to the havoc created by the dogfish, nor to the grease with which the nets are saturated from the herrings, and which rots them rapidly unless they are continually cleaned.

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[1] "Great Yarmouth," &c., London, 1866, pp. 290, 291, 293.

On inquiry at one of the largest manufacturers of nets in Boston, I found, as was naturally to be expected, that the net makers use catechu in a very different way from the fishermen; that is to say, they fix it methodically with bichromate of potash, as would be done at a dye-house in the case of any other cotton or linen goods. By the manufacturers, the nets are steeped in a hot aqueous solution of catechu and then treated to a bath of the bichromate, whereby the color is oxidised, darkened, and "fastened" to the twine in the manner familiar to dyers. It is a process that has to be managed with care, lest the netting should be weakened. Extract of hemlock bark, they told me, might be used instead of catechu, but it would cost more. It is only the lighter nets, such as herring nets, that are stained with catechu in Boston. The heavier nets are tarred; and, according to my informant, his firm tar many more nets than they tan. It did not appear that tar and catechu are used together by the Boston dealers, as they are in some places.

It is a fact well known to dyers that linen and cotton can be stained, after a fashion, by the use of tanning materials even when no mordant is present. Bancroft[1] says: "There is a species of coloring matter diffused in greater or lesser proportions through the barks and other parts of almost all trees and shrubs, and which, without any basis or mordant, permanently dyes or stains wool, silk, cotton, and linen, of that particular kind of color which the French call *fauve* (fawn color), and sometimes *couleur de racine ou de noisette* (root or hazel-nut color). . . It is found most abundantly in the peelings, rinds, or husks of walnuts, in the roots of walnut trees, in alder bark, &c.; and it seems to acquire both body and permanency by attracting and combining with pure air." Domestic processes of dyeing cotton, in this sense, by simply soaking in tan liquor and ageing, are sometimes mentioned in the agricultural newspapers.[1] But in spite of this familiar knowledge, it would still be remarkable if so dark and so durable a color as is actually seen on the sails in some regions had been imparted to them by merely soaking or boiling the canvas in tan liquor. As bearing upon this point, I may cite the following sufficiently explicit statement from a very old authority.[2] For the sake of enforcing the contrast between cotton and wool the author premises that "vegetable filaments, and thread and cloth prepared from them, differ remarkably from wool, hair, silk, and other animal productions, . . . in their disposition to imbibe coloring matters." And in illustration of the fact, a special instance is noted, as follows:—"Fishing nets are usually boiled with oak bark or other like astringents, which render them more lasting. Those made of flax receive from this decoction a brownish color, which, by the repeated alternations of water and air, is in a little time discharged, whilst the fine glossy brown communicated by the same means to silken nets permanently resists both the air and the water, and stands as long as the animal filaments themselves."

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[1] "Philosophy of Permanent Colors," **1**, 227 of the Philadelphia edition of 1814.

Tannin of one kind or another is actually employed by dyers, not so much, perhaps, for the sake of the color it imparts by itself, as that it serves as a mordant to fix colors on cotton and flax, which could not otherwise be so well employed on these kinds of fibres. Crace Calvert,[3] for example, says of sumac that it is largely used in Yorkshire to mordant the cotton warps of mixed goods. By means of it the cotton takes the same colors as the woolen weft with vegetable dye-stuffs and with aniline colors. But it is particularly under the influence of weak alkalies that the tannins combine with vegetable fibres, and that they absorb oxygen, turn brown, and become fixed upon the cloth. As Calvert has said, on p. 311 of the work just cited, all the tannins are remarkable for the avidity with which they absorb oxygen in presence of alkalies, being converted into bodies of various colors, green, red, brown, and black.

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[1] See, for example, "The Rural New-Yorker," Jan. 31, 1880, p. 80, and May 14, 1881, p. 327; also, "The Cultivator and Country Gentleman" (Albany), 1880, **45**, 431.

[2] The chemical works of Casper Neumann, abridged by Wm. Lewis, London, 1759, p. 429 note.

[3] "Dyeing and Calico Printing," Manchester, 1876, p. 326.

I find, on investigation, that methods of dyeing depending on the action of alkalies upon tannin have long been in familiar domestic use in this country; the bark of the maple, alder, chestnut, walnut, and butternut, and doubtless of other trees, being used in different localities, as well as the husks of several kinds of nuts. For example, L. Stanley, of Maine,[1] directs: "To color brown, make a dye of common alder bark. First dip the articles in this, then wring them out and dip them into weak lye. This will make the color light or dark, according to the strength of the alder dye. It is a fast color." In the "American Agriculturist" for January, 1869, two or three receipts for dyeing tan-color are given. In general, the directions are to boil black-walnut hulls to a strong liquor, into which either cotton or woollen yarn may be put and boiled for ten minutes. The yarn is then taken out and dipped in a pail of strong lime-water, and the operation repeated until the color suits; or, instead of the hulls, chestnut or walnut bark may be used, or extract of hemlock bark.[2] According to Porcher,[3] "the inner bark of the short-leaved pine (*P. tæda*) will dye cotton goods a brown color without the aid of copperas. After boiling in the solution, dip in strong lye." I have heard of alder bark and soft soap being used in domestic dyeing in Nova Scotia for coloring linen tan-color; and it is plain that the soap would exert an alkaline action in this case, even if it served no other purpose. It appears from all this that while tan liquor alone is undoubtedly used in some localities for staining canvas and twine, there are other places where the people are familiar with a true process of dyeing, dependent upon the use of alkalies in conjunction with decoctions of astringent barks. As will be seen directly, I have discovered one locality where the last-named system is said to be applied to the coloring of sails and nets.

After having been for forty years accustomed to the sight of tanned sails, and familiar with the sailor's belief that they are simply tanned as leather is, but without ever having been thrown into intimate contact with people who use tanned sails, I had the curiosity in the summer of 1882 to ask a very intelligent fisherman on the New Brunswick coast how his comrades colored their sails, and was not a little surprised on being told of processes which, when chemically considered, mark a distinct advance on the traditional sytem of simple soaking in tan liquor. The New Brunswicker told me that his people boil the bark of spruce or fir trees in water for many hours, and finally decant the cooled liquor into a tub, where it is mixed with soft soap or with saleratus, and the sail (either hemp or cotton) is put to soak in the mixture for a couple of days. He maintained that sails thus tanned last two years longer than those not tanned, while for nets the process is deemed to be wellnigh indispensable. On my asking whether they didn't use oil with the saleratus, he answered that they did; and it was this reference to the use of oil and alkali which excited my interest in the subject, and led me to search for testimony which should corroborate his statement. It is evident from what has gone before, that in so far as relates to the use of alkalies with the tan liquor, the statements of the New Brunswick fisherman are fully supported. I have found evidence that both "lye" and soft soap are familiarly used as adjuncts to dyeing with barks, and it is well known that the conjoined use of tannin and alkali is an approved mode of operating which has long been habitual, in one form or another, in dyehouses. I have been assured, moreover, that soft soap is used in some Nova Scotian households in dyeing wool with cudbear, "to set the color and change its shade," which goes to show a practical familiarity with the use of this agent in coloring processes.

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[1] American Agriculturist, February 1867, **26**, 48.

[2] *Ibid.* Nov. 1868, p. 401.

[3] "Resources of the Southern Fields and Forests," p. 585; cf. pp. 215 and 217.

It should be explicitly said, perhaps, that I have not the least doubt that my informant was a thoroughly trustworthy person. I fully accept his statements as to the use of saleratus and soap; though of course he may have failed, and probably did fail, to correctly state certain details of the process as to ageing, dipping, and drying; but it will be noticed that in our conversation the word "oil" was first suggested by myself, and there is unquestionably a certain risk that we may have misunderstood one another in respect to this particular item. If oil is really used, as he said it was, in the process of coloring sails, the fact is one of no little interest in its archaeological bearings; it would be an important contribution to the history of chemical technology, for, considered merely as a method of dyeing, the process would then be essentially identical with the famous old East Indian method of fixing a fast red on cotton by means of madder (or its equivalent) and an oil mordant:

I mean the color known to the English as Turkey red, and to the French as *rouge d'Andrinople.* The East Indian process, as described by the earlier investigators, is as follows: "For dyeing cotton, the Hindoos prepare an imperfect soap from oil, ashes, and animal matters. More precisely, they soak the skeins in a soapy liquor made with goat dung, oil (of stated kinds), and potash lye, obtained by leaching the ashes of certain plants; then they expose the cotton to sun and air for several days, and finally dye it with chay root (equivalent to madder), without applying previously to the cotton any alum, or acid, or saline matter."[1]

To my own mind, the verisimilitude, or, so to say, the chemical reasonableness, of the story as related to me by the New Brunswick fisherman lent strength to it, and I would have been glad to have found recorded evidence to support it, but, as has been seen already, I have practically failed to do so. It is to be noticed, meanwhile, that the soft soap employed by the New Brunswickers would naturally be of home manufacture and incompletely finished. It would be likely to contain of itself much of the emulsion of oil and alkali so useful in Turkey-red dyeing. The probabilities are strong withal that the soap is made from a more or less rancid fish oil such as Pallas[2] found in use among the Armenian dyers of Turkey red at Astrachan, and such as in more recent times has been approved an efficient agent by the Turkey-red dyers of Manchester.

In case it should turn out to be true that sails and nets are anywhere colored by means of an oil mordant, it will be of special interest to ascertain how long the process has been in use in the locality, and whence it came thither. It seems highly improbable that the method should have been copied either in America or Great Britain from the Turkey-red dyers, for it is only in recent times, comparatively speaking, that the process of dyeing Turkey red has been practised by the Western nations. It was not until the middle of the eighteenth century that it was successfully employed in France.[3] Mention is made of it as being employed in 1765, and it is admitted that the art has been successfully practised in Great Britain since 1785.[4] The details of the Turkey-red process, as imported to civilized Europe, were so tedious and complicated, and the scientific explanation of them was so little understood, that there is hardly the least likelihood that any feature of the process could have been transmitted by professional dyers to European and American fishermen or housewives in recent times. The very crudeness of the domestic processes above-mentioned would of itself indicate that they have not been derived from any modern dye-house. It seems far more probable that the tanning process might have originated in a primitive state of society, where the oil mordant may have been used familiarly, not only for red but for various other colors. It is in evidence that, though comparatively rarely used by the Western nations for fixing other colors than red, the oil mordant is perfectly competent to be used with a variety of other dyes beside madder and its congeners. Laugier[1] has dwelt upon the general applicability of the process for dyeing hemp, flax, and cotton. He finds it particularly applicable for yellows, for instance, as well as for reds. Beautiful shades of purple have been fixed upon cotton cloth by first mordanting with oil, as in the Turkey-red process, and then dyeing with aniline purple.[2] Indeed, the ordinary operation of "galling," employed incidentally in Turkey-red dyeing to strengthen and modify the red color, would be practically a dyeing of the cloth tan-color if it were pushed far enough. It is manifestly closely analogous to the dyeing of sails as described to me by the New Brunswick fisherman. It is known that under the influence of weak alkalies and dampness, galled cloth may absorb oxygen from the air and take on a brown color which is highly undesirable from the point of view of theTurkey red dyers. Chaptal[3] stated the matter many years since: "The astringent principle of the nut-galls unites with the oil and forms a compound which darkens on drying and is but slightly soluble in water." "It is better to choose a dry time for the process of galling, because damp air blackens the astringent principle. After having been galled, the cotton cloth should be dried promptly, in order to avoid the blackening which would injure the brightness of the red the dyer wishes to obtain." Lewis[4] long ago tried experiments on fixing blacks by means of an oil mordant, using soft soap and following Mazeas's directions. He appears to have obtained a tolerably good fixation, though his colors were not handsome. The oil mordant was formerly sometimes used also for preparing a color known as "Swiss pink."

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[1] Mazeas, Memoires des Savans étrangèrs, 1763, **4**, 15-18.

[2] Cited by Berthollet, Elemens de l'Art de la Teinture, **2**, 161.

[3] Ure, Dict. Arts, **2**, 90.

[4] McPherson's Annals of Commerce, **3**, 433, and **4**, 95.

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[1] Dingler's Polytechnisches Journal, **47**, 278.

[2] Watts's Dictionary of Chemistry, **2**, 357; Reports by the Juries: International Exhibition of 1862, Class XXIII, p. 3. It is to be hoped that the yachtsman who may set topsails of this superb color and strive to carry them to the forefront will gain a more worthy renown than did his prototype at Actium.

[3] Memoires de l'Institut (An. VII), **2**, 291, 292.

[4] In his "Philosophical Commerce of the Arts," London, 1763, **2**, 431.

In some localities fishermen preserve their nets and sails by the combined use of bark (or catechu), tar, and oil (or grease), and the process has specially interested me as possibly having some bearing upon the question of an oil mordant just now discussed. Thus, in the Encyclopædia Britannica, article Fisheries, p. 248 (of the edition of 1879), it is stated that "barking" the sails is a regular practice with the trawlers, as it is with most other fishermen in England and Scotland. The process consists in mopping them over with a composition of a solution of oak bark, tar, grease, and ochre, which acts as a good preservative of the canvas. This is done once in six or eight weeks, and a suitable place is kept for the purpose at all the important fishing stations. Captain J. W. Collins[1] states that to preserve their nets, the Newfoundland cod fishermen make a mixture of tan and tar, which is thought better than either used separately. The tan is made from spruce buds, fir bark, and birch bark (hemlock bark is not used), which are boiled together until it is sufficiently strong, when the bark is removed and tar added in the proportion of five gallons tar to two hundred gallons tan, the whole being stirred well together. Some care is necessary in applying this or else it will not be evenly distributed on the net. The custom of mixing tan and tar has doubtless been introduced from England, as it is known that the Cornish fishermen do this, pouring out their tanning liquor into large vats with coal tar, and this mixture is found to preserve the nets much longer than simple tanning. The Newfoundland nets when prepared in this manner generally last about four seasons.

Something similar is done by the Irish fishermen from Galway, a colony of whom have for a number of years been settled here at South Boston. I have received information from three different individuals with regard to the methods employed. The first witness assured a friend of mine that his people use "catechu, grease, and tar, to color their sails." He had himself forsaken the traditional practice and "would not himself put such stuff on a white sail." Some time afterward I had an opportunity to talk with an intelligent Galway woman, a domestic in a friend's house. I quote her words: "First they take the clean cloth. Then it is all white. Then they get some kind of oil, I don't know what, and get it all over the cloth, and then they hang it up to dry for a long while—a week or two weeks—and then the cloth is yellow, and then they put the oil on it again and hang it up to dry again—and I don't know what they do after that." I was careful not to ask any leading question, and made no effort to help on the story. She knew very well that the sails were almost black finally, but could not tell what made them black. Still later this same woman obtained the following account from the mouth of an old Galway fisherman. Take three gallons of tar and twenty pounds of fresh butter. Melt the butter in a vessel and add to it a cup of salt. If salt butter were used there would be no need of the salt. Heat the tar almost to boiling in another vessel, and slowly add to it the butter, constantly stirring meanwhile. When the two are thoroughly combined the mixture is applied to the sailcloth by the hands of the fishermen; generally six fishermen on each side of the sail. The rubbing-in by hand is deemed to be all-important, and it is commonly done in the early morning of a fine day, and the sail exposed to the sun in order that the mixture may be dried in. In good sunshiny weather the drying process is completed by sundown. At the end of a week another coating is given in the same manner, and after a couple of days the sail is fit for use. The quantity of tar and butter above given is sufficient for one of their fishing boats, which are some six or eight tons burthen. Great importance is attached both to the rubbing in and the drying. In connection with these stories I could but recall the fact that the old French name of tarred cloth was *toile grasse*.

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[1] Bulletin of the U. S. Fish Commission, 1881, **1**, 7.

In this category may be mentioned the Dutch method of tanning cotton herring nets, as described by Capt. Collins,[1] and stated by him to be "thought better than any other by these foreign fishermen." The tan is made by boiling catechu in water, in the proportion of one pound of the former to two and a half gallons of the latter. When it is sufficiently strong, the nets are soaked in it twenty-four hours and then dried. They are tanned and dried three times, and then soaked in linseed oil. A pound of oil is provided for each pound of net, and the nets are allowed to remain in the oil as long as any of it will be absorbed. They are then well drained and spread on the ground to dry, after which the process is completed by tanning them once more. Nall[1] says a strong three-twist cotton cord procured from Musselburgh has lately been introduced as an experiment. It is prepared by steeping in a mixture of linseed oil and varnish and is then squeezed through rollers. This renders it stiff and smooth as wire when dried. It is afterwards subjected to the tanning process. In addition to hempen twine, a coarse Persian silk was employed in the netting used in the Dutch fisheries of the 17th century, as more durable. It was slightly pitched or exposed to the smoke of burning ash to acquire a dark color and render it less perceptible by the fish. There is a process of varnishing the silken lines used by pleasure fishermen for the purpose of keeping them dry and reelable that differs from the foregoing. As described by de la Blanchère, in his Dictionary, p. 765, the lines may either be boiled in a drying oil, or, better, a small quantity of drying oil with which some white and green paint has been mixed may be carefully rubbed upon and into the stretched line. A second coating of the varnish is laid on when the first has become dry, and the operation is repeated at intervals until the wished-for stiffness and impermeability have been obtained. De la Blanchère remarks, also, that nets are sometimes treated with tars obtained from coal, and that the fishermen commend coal tar for this purpose in certain cases, in spite of the black color and the penetrating odor it imparts to the nets. John M. Mitchell[2] reports that Irish nets are most frequently tarred instead of being barked. Tarred nets, he says, are not so durable; in direct opposition to which statement I found a strong feeling at Provincetown in favor of tar as being a much better preservative of nets than tan. Capt. Atwood was decidedly of this opinion. Until the war of the rebellion his townspeople were accustomed to use pine tar from the South; it was only when their supply of the material was cut off that they began to use coal tar. One of the Nova Scotian fishermen with whom I talked about tanning nets laid a good deal of stress on the large amount of "gum" there was in the fir bark employed. Both he and Capt. Atwood seemed to believe that this resinous matter played an important part in preserving the nets. The Boston manufacturer of nets previously alluded to said that his firm formerly used Wilmington tar, but now they used coal tar altogether. He urged that tar makes the net stronger, that it makes the twine more like wire, that it hardens the fibres and keeps them together so that the twine does not fray. He had heard of tar and oil being used together, linseed oil he supposed, and thought the purpose of the oil might be to soften the tar. He remarked on having no facilities for drying (ageing) the tarred nets in his Boston warehouse, and dwelt upon the fact that freshly tarred nets are liable to "heat" and spoil. To prevent them from suffering injury in this way it is customary to soak them in brine. Moreover, when tarred nets are done up into bales, salt is scattered upon each layer of the netting to hinder the package from heating. It appears that it is now customary with the fishermen on the New England coast to regularly salt down their nets when they are stowed away at the end of the fishing season. In warm weather also the mackerel fishermen are at pains to strew salt upon their nets, layer by layer, when they stow them, even for brief periods, in the seine boats; the idea being, of course, in this case to check the putrefaction of the slime and gurry with which the nets are soiled.[1]

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[1] Bulletin of U. S. Fish Commission, 1881, **1**, 8.

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[1] In his "Great Yarmouth," &c., London, 1866, p. 291, and 290 note.

[2] In his book "The Herring," Edinburgh, 1864, p. 99.

As to other methods of protecting sails from mildew, I learn that burnettising (*i. e.* the use of a dilute aqueous solution of chloride of zinc) is sometimes practised in this vicinity. I was assured by the captain of a sea-going schooner that once when a suit of his vessel's sails seemed ruined with mildew he had them dipped, with the result that they came out white and clean, and wore well for three years. One practice is to spread out the sails of small vessels on a beach and wash them over with a mixture of whitewash and brine. Some people appear to use plain whitewash. An objection is urged, however, to the use of lime that it tends to rot the canvas, and there is probably some risk that in seeking to destroy the mildew fungus with alkalies, the growth of forms favorable for putrefaction may be promoted. To quote from Duclaux:[2] "Acid liquids are in general more favorable to moulds, to yeasts, and to mycoderms; it is only very exceptionally and only *en passant* that mobile forms are found in them, *i. e.* vibrios, bacteria, or monads. These kinds appear, on the contrary, by preference, in neutral or alkaline liquids, where the moulds for their part have much trouble to live. The mould Aspergillus, for example, grows freely on bread moistened with vinegar, on the juice of lemon or slices of lemon, and on sour fruits and liquors."

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[1] The modicum of truth in the old conception that "putrescent bodies exert an action on complex organisations which by themselves are not putrescent," is well illustrated by a case like this. A parcel of microdemes having established a satisfactory residence upon the animal matter with which a net is soiled, soon find the cellulose of the twine a useful addition to their food. It serves in some sort as a diluent of the highly nitrogenised ration which the slime supplies. In other words, some of the constituents of the cellulose of the fibre are involved in the reactions which occur during the fermentation, and the integrity of the twine suffers accordingly.

[2] E. Duclaux, "Ferments et Maladies," Paris, 1882, pp. 43, 45, 50.

I find a common impression that the sizing in new canvas attracts mildew, *i. e.* that the mildew fungus finds a fit field for its support in the sizing which has been introduced into the interstices of the canvas at the factory. To avoid this difficulty some owners of vessels prefer to bend their new sails in the autumn in order that the sizing may be "worked out" of the canvas by the autumn and winter rains, at a time, that is to say, when the weather is too cold for mildew to prosper. Old sails are said to be comparatively exempt from mildew. The time-honored and universal custom of shaking out or hoisting sails in order that they may dry after rain is one familiar method of preservation. It is precisely because drying is frequently impracticable in some climates that the tanning process is practised.

It would be well to study practically whether the method of permanently dyeing sails, either with the aid of an alkali or by means of an oil mordant, is really an effective means of shielding the canvas from the mildew fungus; and it would be of interest to determine whether the altered and oxidised oil that constitutes the mordant in Turkey-red dyeing might not of itself help to preserve sails, even if no tanning or other coloring substance were combined with it. This last question could perhaps be answered at once, even now, by persons who have had experience with the use of Turkey red cloths in damp situations. It is not unfair to suppose that the oil mordant might be useful of itself, since it would probably tend to keep the sails drier than they would be in its absence; and in this way it might be obnoxious to the fungi, which need moisture in order that they may thrive. So too with cordage; it might be questioned whether ropes made from hemp that has been impregnated with the oil mordant (and tannin), instead of with tar, would not be specially serviceable in some cases.

BUSSEY INSTITUTION (OF HARVARD UNIVERSITY), *August*, 1883.

REVIEWS AND REPORTS.

Report on Analytical Chemistry.

Sulphur.—A test for hydrogen sulphide.—Emil Fischer[1] recommends for the detection of hydrogen sulphide, its reaction with para-amido-dimethyl aniline and ferric chloride, by which H. Caro showed that methylene blue is produced. In order to detect very small quantities of hydrogen sulphide in aqueous solution, it is treated with about $\frac{1}{50}$ of its volume of fuming hydrochloric acid, a few grains of sulphate of p-amido-dimethyl aniline, and, as soon as this is dissolved, a drop or two of dilute ferric chloride. If hydrogen sulphide is present the solution becomes clear blue after a short time and the color is permanent. The addition of hydrochloric acid prevents the formation of a red dye by ferric chloride and amido-dimethyl aniline which is formed in neutral or weakly acid solution. It is possible to detect, in this way, 0.000018 gram of hydrogen sulphide in a litre of water, where neither lead acetate nor sodium nitro-prussiate gives a reaction.

P-amido-dimethyl aniline may be prepared very readily from the dye "helianthine" by reduction with zinc dust and hydrochloric acid, or by ammonium sulphide.

The detection of free sulphuric acid in the presence of aluminium sulphate.—Oscar Miller[2] shows that methyl orange not only furnishes a test for free sulphuric acid in presence of aluminium sulphate, but also admits of its determination with methyl orange as indicator. 0.01 gram of free acid has been detected in 1 litre of water containing also 0.645 gram aluminium sulphate. Ethyl orange is also very sensitive towards free sulphuric acid, but is also colored rose-red by neutral aluminium sulphate.

Nitrogen.—A new method for the determination of nitrogen in organic substances has been proposed by J. Kjehldahl.[3] The method is somewhat similar in principle to that proposed by Wanklyn as a modification of his albuminoid ammonia process in water analysis. By Wanklyn's method the nitrogenous substance is oxidised by potassium permanganate in alkaline solution. In the method now proposed by Kjehldahl, the oxidation is accomplished by the same reagent, but in strongly acid solution. The substance is heated for some time with an excess of concentrated sulphuric acid, to near the boiling point; the solution thus obtained is oxidised by adding an excess of dry powdered potassium permanganate. Under these conditions the nitrogen of organic substances in general is converted into ammonium sulphate, from which the ammonia is distilled, after supersaturation with caustic soda, and determined by titration in the ordinary way. The essential conditions, under which the process admits of satisfactory results, are, that ammonium sulphate suffers no decomposition at the high temperature used, nor in the subsequent oxidation, and that the energetic phenomena which accompany the oxidation can be regulated so as to avoid loss of substance. The details of the process are simple and admit of many analyses in a day. The substance is weighed off in a small flask in which the oxidation is to be performed. The amount of sulphuric acid to be added may vary between moderate limits, but about 10 cubic centimeters are generally used. This is added to the flask and the whole heated for about two hours until all reaction has ceased. The potassium permanganate in powder is added slowly in a small but constant stream, and in a few minutes a dark green color shows the oxidation to be complete. After cooling, the liquid is diluted with water and removed to a flask holding ¾ litre, where, after the addition of caustic soda, the ammonia is distilled off into an absorption bulb and estimated with standard acid. Small pieces of zinc are added to the distilling flask to prevent the violent, irregular boiling always noticed when ammonia is distilled.

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[1] Berichte der deutschen chemischen Gesellschaft, **16**, 2234.

[2] *Ibid.* 1991.

[3] Zeitschrift für analytische Chemie, **22**, 366.

For titrating the ammonia or the excess of standard acid in the absorption apparatus, any of the ordinary methods may be used, but the author recommends particularly the method based on the fact that a mixture of potassium iodate and iodide yields free iodine with an acid, which may be titrated with sodium hyposulphite and starch paste, with such sharpness as to make the method preferable to any other when ammonia is to be determined from substances containing only a very small percentage of nitrogen.

A list of analyses of various organic substances by this method indicates that it is capable of very exact results, but is not applicable to substances containing nitrogen in the form of volatile acids, as the cyanogen compounds or oxides of nitrogen. With a few alkaloids, notably quinine, the entire nitrogen is not evolved.

Determination of ammonia in plant juices and extracts.—Two methods are in use for the estimation of the ammonia in plants: either the liquid is treated with milk of lime and the ammonia taken up in titrated acid as it evaporates (Schlösing's method), or it is distilled with magnesia. E. Bosshard[1] has shown, however, that when asparagine or glutamine is present in plant extracts, the results are too high. If these amides are removed by Schulze's method of precipitating with nitrate of mercury the results are too low. But by precipitating the ammonia with phospho-tungstic acid and distilling the finely divided precipitate with magnesia, satisfactory results are obtained. The extract is acidified with hydrochloric or sulphuric acid, then treated with phospho-tungstic acid in excess, and filtered after one or two hours. That part of the precipitate which adheres to the glass is dissolved off by hot water and added together with the filter to the distillation flask, magnesia added and the determination made as usual.

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[1] Zeitschrift für analytische Chemie, 22, 329.

A new method for the estimation of minute quantities of carbon.[1] By J. E. Stead. The method depends on the fact that the carbon present in iron and steel is soluble in a solution of caustic soda, and can be determined by the depth of color which it imparts to the latter. A specimen of iron is dissolved in nitric acid and treated with caustic soda of a certain strength. The colorimetric estimation of the carbon is then effected by comparing the depth of color with that of different lengths of a standard solution. It is shown that the carbon is not oxidised when boiled with nitric acid even after the complete solution of the iron. The author recommends a special form of apparatus for the colorimetric test.

Alkalimetry.—J. Wieland[2] has made a comparative study of the various indicators for the detection of free acids and alkalies. Ethyl-orange is, according to Wieland's results, the most sensitive indicator known; and it also exceeds other indicators in the sharpness of its change in color. The following scheme represents the various indicators in the order of their delicacy. The numbers representing the sensitiveness indicate the number of cubic centimeters of hundredth normal acid or alkali necessary to cause a change of color in 50 cc. of a solution containing 2 drops of a .05 per cent. solution of the indicator.

I. Not affected by CO_2.	Change of color by titrating an alkali with an acid.	Sensitiveness toward	
		Acids.	Alkalies.
Ethyl-orange,	Orange to rose color.	0.3–0.5	...
Methyl-orange,	Yellow to orange. " to rose.	0.3–0.5	...
Phenacetolin,	Brown-red to yellow-green,	0.3	0.3 Na_2CO_3
Sodium alizarinsulphonate,	With KOH, red to orange. With Na_2CO_3, red to yellow.	0.1	0.6
Cochineal,	Blue-red to yellow-red.	...	0.3
Tropäolin, OO,	Yellow to orange.	Not very sensitive.	
Fluoresceïn,	Loses fluorescence.		
II. Affected by CO_2.			
Nitrophenol,	Yellow to colorless.	...	0.5
Phenol phthaleïn,	Blue to colorless.	...	1.5–2.0
Flavescin,	Yellow to colorless.	...	0.5–1.0
Alizarin,	Blue-red to yellow.	0.3	...
Litmus after Kretschmar,	Blue to yellow-red.	0.5	...
Pararosolic acid,	Red to yellow.	...	0.6
Eupittonic acid,	Blue to brown-red.	...	0-9
Rosolic acid (coraline),	Blue-red to red.	...	0.6

The brackets indicate those nearly the same in the sharpness of the change.

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[1] Chemical News, **47**, 285.

[2] Berichte der deutschen chemischen Gesellschaft, **16**, 1989.

Iron.—Zimmermann has shown that Margueritte's method for determining iron by potassium permanganate can be used in the presence of hydrochloric acid if manganese sulphate is added. It is now shown by J. Krutwig and A. Cocheteux[1] that the manganese sulphate may be omitted if precautions are taken: 1, to use as little hydrochloric acid as possible for the solution of the iron (10 cc. for .1 gram iron ore); 2, to reduce with zinc in the hydrochloric acid solution; 3, to add twice as much sulphuric acid as there is hydrochloric acid present; 4, to dilute the solution to 300 cc. and to use a dilute permanganate solution for the titration.

Petroleum.—F. Beilstein[2] has made a comparative study of the various forms of apparatus which have been proposed for determining the inflammability of petroleum by means of its flashing point. The forms of apparatus of Abel, Engler and others give concordant results under proper management, but require that the instruments be constructed exactly alike, or two instruments of the same make will give different results. Thus two specimens of Engler's apparatus apparently of the same dimensions gave a difference of 2°. The reason for this was, that the marks to which the petroleum is to be poured were not at the same level. Liebermann's method is the only one which is free from these objections. The results in this case are independent of the amount of petroleum and of the air passed through, as has been verified by Stoddard. Stoddard's apparatus consists of a cylinder 2–3 cm. wide and 10–12 cm. long, open at top and closed by a cork below, which admits a glass tube for forcing air through the petroleum which fills the cylinder to one-third its height. The cylinder is placed in a water-bath, air forced through, until a light held at the mouth ignites the vapor.

Beilstein shows that the flashing point in this apparatus varies with the width of the cylinder, and that this must always be to the height as 1 to 5 or 7. When volatile oils are present in the petroleum the result is affected by the time during which air is passed through. After studying all the conditions which affect the determination of the flashing point, the author adopts the following method as capable of most concordant results. An ordinary glass cylinder 35 mm. wide and 175 mm. high, has a mark 60 mm. from the bottom and a second at 70 mm. from the bottom. The petroleum is poured in to the lower mark. Air is passed through by a doubly bent tube which has a rose formed end to subdivide the air bubbles. The cylinder is placed in a water-bath the temperature of which is raised slowly (one degree in two or three minutes). At each degree air is passed through for five seconds, so rapidly that the foam from the petroleum reaches the second division. At the same time a small flame is held at the mouth of the vessel. The first determination gives only approximate results. The petroleum must be replaced by a fresh supply, the observations are then begun at the temperature obtained in the first determination. If the petroleum is not heated too rapidly so that the temperature of the bath outside the cylinder is only about one degree higher than that within, the difference between single determinations need not be greater than ¼ degree.

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[1] Berichte der deutschen chemischen Gesellschaft, **16**, 1534.

[2] Zeitschrift für analytische Chemie, **22**, 309.

The method of determining the safety of oil by its flashing point gives no indication of the actual value of the oil for use in lamps. Petroleum which is rich in heavy oils shows, naturally, a satisfactory flashing point, but cannot be used in ordinary lamps. Distillation is the only method by which the nature of petroleum can be determined from all points of view. In order to obtain concordant results by distillation, certain precautions are necessary, which may be best fulfilled by the following process. A round flask provided with a Glinsky's dephlegmator is weighed, then the petroleum added and weighed again. The distillates are collected in a weighed receiver after passing through a tube ¾ meter long without a condenser. The distillation is so conducted that about two grams distil in a minute. The distillate below 150° is weighed as light oil, that from 150°–270° as oil suitable for burning purposes, and the residue in the distilling flask weighed when the temperature reaches 270°. The amount of heavy oil boiling above 270° must be less than 15 per cent. of the entire oil, although this may go higher in Caucasian petroleum. If the light oil is less than five per cent. the oil may be regarded as safe.

Methyl aldehyde.—L. Legler[1] proposes a method for determining methyl aldehyde which is based upon the following reaction with ammonia:

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

The reaction takes place even with dilute solutions of ammonia, and is completed in a short time without the formation of any secondary products. The solution containing methyl aldehyde is titrated with an excess of a standard ammonia solution, and this is titrated again with normal sulphuric acid. With alkalies the reaction is:

$$2CH_2O + NaOH = HCOONa + CH_3OH,$$

which is also capable of yielding concordant results, but it is necessary to warm the solution for some time before the reaction is complete, and if the mixture is heated rapidly the results are too low.

As methyl aldehyde shows little tendency to transformation into formic acid in neutral or acid solution, it may be determined in presence of volatile acids by determining the sum of the acids and methyl aldehyde by titration with ammonia; sulphuric acid is then added, and by repeated distillation the volatile acids and methyl aldehydes obtained in the distillate, the acids are then titrated with normal alkali, and the difference between this result and the ammonia titration gives the methyl aldehyde. Similarly, methyl aldehyde may be estimated in presence of formic and acetic acids. The acids are first determined by titration with cold normal alkali. The methyl aldehyde is then converted into formic acid by heating with alkali, and the total amount of formic acid determined, the difference gives the amount of acetic acid.

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[1] Berichte der deutschen chemischen Gesellschaft, **16**, 1333.

The detection of urea in aqueous solution.—C. L. Bloxam[1] recommends acidifying the solution with hydrochloric acid, and evaporating on a crucible lid till thick white fumes are no longer evolved. The residue is dissolved in a drop or two of ammonia, and a drop of barium chloride added. By stirring with a glass rod, barium cyanurate is formed on the lines of friction made by the glass rod. A very characteristic test for the cyanuric acid consists in dissolving it in a drop or two of ammonia, and adding a drop of a weak solution of copper sulphate; on standing for a few minutes, a violet-colored crystalline precipitate separates. This seems to be cuprammonium cyanurate described by Wöhler.

D. T. D.

RELATIONS OF CRYSTALLOGRAPHY TO CHEMISTRY.

Since it is now generally conceded that the description of no new chemical substance is altogether complete without a thorough crystallographic and optical examination of its crystals, it may not be amiss to present here a concise statement of the results already obtained in this field by German investigators, particularly from the study of the crystals of organic compounds. It has been thought that, by indicating the questions open for solution and the general end toward which such investigations are tending, an incentive might be offered to those not already conversant with them to undertake similar work in this country, where as yet little of the kind has been done.

All that has recently been accomplished by physicists and mineralogists to explain the hidden relation between the outward form and physical properties of crystals has done much to clearly bring out that still deeper mystery, the solution of which may well be regarded as the end and aim of theoretical mineralogy, viz. *The manner in which both the crystalline form and physical properties of substances are directly dependent upon their chemical constitution.* This is a question of which we as yet know very little, but it is the one upon which the work in chemical crystallography abroad is being directed, and it is one whose importance warrants the vast number of observations which must precede its solution.

The first important discovery to throw much light upon the relation between crystalline form and chemical constitution was that by

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[1] Chemical News, 47, 285.

Mitscherlich, in 1819, of isomorphism and polymorphism. It was found that different substances of analogous chemical composition possess very similar crystalline forms, and can even unite in forming a single crystal; but that, on the other hand, the same chemical substance sometimes exhibits two or three quite distinct forms, which might even belong to different crystal systems. It was hoped that these two laws, which had yielded such excellent results in inorganic chemistry and mineralogy, would prove still more useful when applied to organic compounds, which allowed of a much more satisfactory study of their atomic and molecular structure than the inorganic, but this hope was not realised. The careful investigation of various isomeric substances as well as those forming a series, whose members differ by CH_2, revealed some similar crystal forms, but even more that were totally unlike. Nowhere could any law or order be discovered. The arrangement of the atoms in an organic molecule is evidently very different from that of the metals, which may be substituted for one another in an isomorphous mixture.

In the year 1870 Paul Groth,[1] then in Berlin, published the results of some crystallographic investigations upon a number of benzene derivatives, which suggested an entirely different direction to be pursued in the study of the crystallography of organic compounds. The question he proposed to himself was the following: Given the crystalline form of an organic compound, what alterations does this form undergo by the substitution of certain atoms or groups for various hydrogen atoms? The study of a series of benzene derivatives, containing hydroxyl (OH), nitryl (NO_2), chlorine (Cl), bromine (Br), and methyl (CH_3), furnished Groth with at least a partial answer to this query, and suggested a working hypothesis, the establishment of which on more general grounds has directed the work in chemical crystallography in Germany during the past twelve years. It was found that the introduction of the hydroxyl or nitro groups into benzene altered the crystalline form only in a moderate degree, and that, too, always in such a way that, while *two* of the axes remained nearly the same, the relative value of only *one* axis and zone were noticeably affected. The effect of the introduction of chlorine (Cl), bromine (Br), and methyl (CH_3) is much more radical. These cause a change of the *crystal system* from one of higher to one of a lower grade of symmetry; but even here the values of the angles of one zone remain unaltered. Groth called this regular change of crystalline form through substitution "morphotropism," and spoke of the "morphotropic power" of an atom or group in reference to the substance in which it was substituted. The morphotropic power was stated to be dependent upon the four following circumstances:

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[1] Monats-Berichte der Berl. Ak. d. Wiss. 1870, 247–258; Poggendorff's Annalen, **141**, 31; Neues Jahrbuch für Mineralogie, etc., 1871, 225.

1. The specific character of the substituting atom or group.
2. The chemical composition of the substance in which the substitution takes place.
3. The crystal system of the original substance.
4. The relative position of the substituting atom or group in the new molecule.

In 1874[1] appeared the results of a crystallographic study of the chlorine and bromine derivatives of naphthalene tetrachloride ($C_{10}H_8Cl_4$) and naphthalene tetrabromide ($C_{10}H_8Br_4$) by C. Hintze, this being a revision of the crystallography of Laurent's paper, "Sur la Série naphtalique," 1850.[2] He verifies the conclusions of Professor Groth in regard to morphotropism, and adds the new fact that different but nearly related atoms, such, for instance, as chlorine and bromine, when substituted in the same position in a molecule, produce very nearly the same morphotropic effects. Such atoms he calls "isomorphotropic." The introduction of chlorine or bromine atoms was found to produce less pronounced changes in the crystalline form of the substances here under consideration than upon that of benzene, thus proving Groth's second condition of morphotropic power.

Two years later[3] Dr. C. Bodewig published his crystallographic investigation of the dinitrobenzene series, the principal result of which was to verify Groth's assertion that the morphotropic power of the nitro-group (NO_2) is slight, and that it is dependent upon the relative position of the group in the molecule (4th condition).

In 1877 Professor Groth, of Strassburg, started the "Zeitschrift für Krystallographie und Mineralogie," a journal having for one of its avowed aims the collection and publication of material throwing any light upon the relation of crystalline form to chemical constitution. This end has been kept well in view, and during the past six years there have appeared in the pages of the "Zeitschrift" the results of a great number of investigations by many different workers in the field of chemical crystallography. These investigations relate partly to connected groups of organic substances and are partly disconnected observations to serve as material for future comparisons. A great variety of compounds are represented, but the results do not yet agree sufficiently to admit of important generalisation.

Up to the year 1877, when the number of organic substances which had been studied was comparatively small, all observations appeared to confirm the laws of morphotropism and isomorphotropism as they had been enunciated by Groth and Hintze. As soon, however, as the number of these observations commenced to increase rapidly, it was discovered that apparent exceptions to these laws were by no means uncommon, showing that, while an excellent beginning had been made, the real mystery to be solved lay far below the depths as yet explored. The necessity of a vast number of observations upon which to base any trustworthy generalisation is at once manifest, so that it cannot be considered strange that no universal law has yet been discovered.

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[1] Poggendorff's Annalen, Erg. Bd. **6**, 1874, 177-198.

[2] Revue scientifique et industrielle.

[3] Poggendorff's Annalen, **158**, 1876, 239-244.

Professor Arzruni[1] first pointed out that morphotropic relations are often wanting just where, from the nature of the substances, they are naturally to be most expected. He also in the same paper shows the uselessness of attempting to explain the crystallographic relations of isomeric substances (often apparently very interesting) before the derivatives of each have been carefully studied. Professor Strüver, of Rome,[2] while studying the derivatives of santonic acid ($C_{15}H_{20}O_4$), came upon a direct exception to Hintze's law of isomorphotropism, and also found that, contrary to expectation, the substances least related chemically showed the greatest crystallographic likeness, *e. g.* santonic acid and metasantonyl chloride are more closely related crystallographically, as are also metasantonic acid and santonyl chloride, than the acids are to their own chlorides.

Dr. O. Lehmann[3] has investigated the subject of physical isomerism. He divides all the chemical compounds which exhibit two or more crystallographically distinct modifications into two classes: 1. Those, *e. g.* ammonium nitrate, whose physical behavior is such as to indicate that the two modifications are composed of physical molecules containing a different number of chemical molecules he calls *polymeric;* 2. Those, *e. g.* paranitrophenol, whose physical behavior is such as to indicate that the two modifications are composed of physical molecules containing the same number of chemical molecules differently arranged he calls *metameric.*

But it is impossible to go into the details of all the more recent investigations, among which but little agreement or order would be discovered. Those specially interested in the subject are referred to the "Zeitschrift für Krystallographie," where synopses of the results published elsewhere will also be found. The gifted mineralogist who first turned crystallographic work in this direction has always maintained a lively interest in its progress, and will, without doubt, embody in his long-promised work on chemical crystallography all the results thus far obtained as well as many suggestions for future work.

In the meantime suffice it to say that a promising field of investigation is here open, offering tempting results to all those who will faithfully and intelligently cultivate it.

G. H. Williams.

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[1] Zeitschrift für Krystallographie, **1**, 434-452. [2] *Ibid.* **2** 588-623. [3] *Ibid.* **1**, 97-131.

PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS. By Ira Remsen. Second Edition, Revised and Enlarged. Philadelphia: Henry C. Lea's Son & Co. 242 pp., 12mo.

In one way or another students of chemistry manage to learn a great many of the facts of the science, but in most cases their knowledge of the underlying principles is sadly defective. They talk glibly enough of atoms and molecules, of "bonds" and "double bonds,"of valence and structure; but if asked some fundamental question, the character of the answer is pretty sure to reveal an unsatisfactory state of mind. This is largely due to the way in which chemistry is commonly taught. Beginners are brought face to face with the deepest subjects with which the most learned chemist can occupy himself. They are made to study certain "cut and dried" statements regarding atoms and bonds, etc., before they have formed any conception in regard to the nature of chemical action; and having once learned some definition of atoms and atomic weights, etc., having once learned to repeat Avogadro's law and the law of Dulong and Petit, they are allowed to go on their way under the fatal impression that they really know something about the subjects. The best of them, if they happen to come under good influences or if they have enough individuality, may recover from the barbarous treatment to which they have been subjected. Many never do recover from it.

The object of the book here noticed is to furnish the student with a logical statement of the connection between the fundamental facts and hypotheses of chemistry, to show how the latter are suggested by the former, and to point out the boundary line between them. It is intended for those who have some knowledge of the facts.

In the first part the methods for determining atomic and molecular weights are treated as fully as is necessary to make the subject clear. Then follow a chapter on the "Properties of the Elements as Functions of their Atomic Weights," and one on "Valence or Atomicity of Elements."

In the second division, which forms the principal part of the book, the much abused, yet important, subject of the Constitution or Structure of Chemical Compounds is taken up. The attempt has been made to show exactly how the prevailing views regarding structure have been evolved from the facts. The formulas in use for the principal compounds are discussed in such a way as to draw attention to the methods involved in constructing them. A careful study of this portion should put the student in a condition to see upon what basis the formulas in common use rest, and ought to do something towards remedying the serious and prevalent evil of writing formulas "because they are in the book."

The treatise concludes with a short chapter on the Determination of the Constitution of Chemical Compounds by Physical Methods.

THE MEDICAL STUDENT'S MANUAL OF CHEMISTRY. By R. A. Witthaus, A. M., M. D. New York: William Wood & Co. 1883.

This is a well-written book which is evidently the result of a good deal of careful thought. It is much more accurate than the books which are frequently put in the hands of medical students. In the preface occurs this passage: "In the preparation of this Manual the author has striven to produce a work which should contain as much as possible of those portions of special chemistry which are of direct interest to the medical practitioner, and at the same time to exclude so far as possible, without detriment to a proper understanding of the subject, those portions which are of purely technological interest. The descriptions of processes of manufacture are therefore made very brief, while chemical physiology and the chemistry of hygiene, therapeutics, and toxicology have been dwelt upon." There is always more or less danger in teaching elementary chemistry with reference to particular applications to be made of it. The fundamental facts and principles of the science should first be taught in the same broad way to every one beginning the study, no matter what use he may intend to put his knowledge to. In books on chemistry written avowedly for medical students, one is apt to find that principles are often lost sight of or sacrificed for the sake of describing the constituents of some ointment or wash. This kind of fault is by no means characteristic of the book under consideration. Further, the book is readable, which is more than can be said of the average chemical text-book. On the whole, if there must be books on chemistry written for medical students, it is well that there is one as satisfactory as this to recommend to them.

The most original feature in the book is the classification of the elements. They are divided into four classes, as follows:

CLASS I.—*Typical elements.*

CLASS II.—*Elements whose oxides unite with water to form acids, never to form bases. Which do not form oxysalts.*

CLASS III.—*Elements whose oxides unite with water, some to form bases, others to form acids. Which form oxysalts.*

CLASS IV.—*Elements whose oxides unite with water to form bases; never to form acids. Which form oxysalts.*

The typical elements are hydrogen and oxygen, and they are called so, "for the reason that although they differ from each other in many of their properties, they together form the basis of our classification."

Any classification of the elements into distinct families or groups must be imperfect for the reason that one and the same element may under different conditions exhibit quite different properties. In the author's scheme the analogies between oxygen and sulphur, between chromium and sulphur, between vanadium and the members of the phosphorus group, are not taken into account.

The plan of beginning a book with information in regard to the fundamental laws and conceptions of chemistry is one which is very commonly followed, but which is nevertheless surely illogical. It is certain that a beginner cannot comprehend the discussion of such matters, however clearly it may be written. For example, how is the average medical student, or any other student, to understand such statements as: "A radical, or compound radical, is a non-saturated group of atoms which behaves like an atom of an element" . . . . "thus the nitric acid molecule consists of the radical NO_2, combined with the group OH," etc., before he has acquired considerable knowledge of chemical elements and compounds, and of their conduct towards each other? Would it not be better to leave most of this out of a book intended specially for medical students? Similar exception might be taken to the free use of graphic formulas without a sufficiently full explanation of their exact significance. It is of infinitely greater value to the student at the beginning of his career to know that benzene has the composition represented by the formula C_6H_6; that it undergoes certain transformations; that it differs in certain ways from marsh gas and from ethylene, than to know that in speculating upon the nature of this substance chemists have concluded that, for good reasons, the constitution of the body may be expressed by a hexagonal shaped formula. But give the beginner the hexagon and he is apt to feel that he knows something about the compound. He can write the formula, what more can we expect of him?

This is not an imaginary difficulty. To one who comes in daily and hourly contact with students of chemistry it is something very tangible.

NOTES.

Bleaching Powder and Analogous Substances.

Kraut[1] has endeavored to show that the conclusions concerning bleaching powder to which the investigations of Odling and of Lunge and Schäppi have led, are incorrect. Odling's view is that bleaching powder consists principally of a compound $Ca<^{Cl}_{OCl}$. This view is based largely on the fact that all the chlorine can be driven out of bleaching powder by a current of dry carbon dioxide, which would not be the case if part of the chlorine existed simply as chloride of calcium. But Kraut finds that when carbon dioxide and chlorous oxide, Cl_2O, are passed together over basic chloride of calcium, the chlorine is given off, from which he concludes that when carbon dioxide acts on bleaching power it liberates hypochlorous acid, which, with carbon dioxide, decomposes calcium chloride. Further, he finds that a compound with bleaching properties can be made from lithium hydroxide, and the idea of a compound analogous to $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}}$ is inadmissible with a univalent element.

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[1] Annalen der Chemie, **214**, 354.

In reply to these arguments, LUNGE and NAEF[1] show that when basic chloride of calcium is treated with Cl_2O alone, a certain amount of bleaching powder is formed; and on passing carbon dioxide over this, only the chlorine which was in the form of bleaching powder is driven out, the rest remaining as chloride. Further, that when chlorous oxide is passed over pure calcium chloride, some of the latter is converted into bleaching powder, thus: $CaCl_2 + ClOH = CaOCl_2 + HCl$.

This shows incidentally that the surplus of calcium hydroxide which is found in bleaching powder is not an essential feature of the compound, as has frequently been supposed; for, in the experiment above, bleaching powder is made from calcium chloride, and contains no calcium hydroxide whatever. Lunge and Naef next pass a mixture of chlorous oxide and carbon dioxide over pure calcium chloride with the object of finding whether the mixture of gases acts differently from chlorous oxide alone. They find that at first carbon dioxide serves merely to dilute the chlorous oxide and delay its action on calcium chloride. But when bleaching powder has been formed, carbon dioxide decomposes it as before.

These experiments may be explained in two ways, in so far as they concern the effect of carbon dioxide upon bleaching powder. The fact that free chlorine and not hypochlorous acid is evolved is most easily explained by supposing bleaching powder a chemical compound of calcium chloride and hypochlorite with the simple formula $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}}$, and that carbon dioxide substitutes both the chlorine atoms, giving calcium carbonate. By the second supposition, that bleaching powder is a mechanical mixture of calcium chloride and hypochlorite, carbon dioxide must first set free hypochlorous acid, which acts on the calcium chloride portion, producing a second quantity of bleaching powder, and so on until by successive conversions into bleaching powder all the chlorine is exhausted. It would be expected in this view of the reaction that a considerable portion of the chlorine would pass out in the form of Cl_2O, when in reality it is shown by experiments on the point that it is almost entirely free chlorine. The amount of hypochlorous acid liberated is almost vanishingly small, and is due to the extra moisture present, which splits up the compound into $CaCl_2$ and $Ca(OCl)_2$, as in the case where bleaching powder is dissolved in water.

Kraut has stated that lithium hydroxide, when perfectly dry, does not absorb chlorine, and when moist only in the proportion of 2 atoms of chlorine to 4 molecules of LiOH, and that the resulting compound is analogous to bleaching powder. From these statements he argues that a certain amount of hydroxide is essential to compounds like bleaching powder, and that the explanation of Odling fails for a monad element. Lunge and Naef now show that the absorption of chlorine by lithium hydroxide may exceed very considerably the proportion of 2 atoms of chlorine to 4 molecules of LiOH, and that the resulting compound is not analogous to bleaching powder, particularly as it is only decomposed to a slight extent by carbon dioxide, unless the temperature is raised to a point where the compound begins to decompose partly into lithium chloride and oxygen and partly into chloride and chlorate; and even in this case decomposition by carbon dioxide is very small. A considerable proportion of the chlorine goes off as hypochlorous acid. When the lithium compound is allowed to stand in an atmosphere of chlorine for some time it loses a large portion of the hypochlorite, a fact which is only true to a very limited extent with bleaching powder.

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[1] Annalen der Chemie, **219**, 129.

Finally, Lunge and Naef investigate the action of chlorine on barium and strontium hydroxides. With the former they are unable to obtain more than traces of a bleaching compound, but its reactions are like that formed from calcium hydroxide. With strontium, however, they form a compound which is decomposed by carbon dioxide even when cold, with liberation of free chlorine, showing that the bivalent elements tend to form compounds much more analogous to bleaching powder than the compound of lithium.

D. T. D.

Note on Boron.

H. Sainte Claire Deville and Wöhler described under the name of crystallised boron some products which they obtained by reducing boric acid at an elevated temperature with aluminium. These products differed, however, in their composition as well as in their external appearance. The substance they obtained most frequently consisted of regular octahedrons of a yellow or brownish red color. The great brilliancy of the crystals, their refractive power, and their hardness resembled the diamond. They contained, however, variable proportions of carbon and aluminium. These crystals were always accompanied by a black substance having a brilliant lustre, sometimes occurring in the form of large plates or scales, transparent only in the thinnest slices. An analysis showed that they contained 2.4 per cent of carbon.

M. Hampe,[1] having studied the crystallised products known as adamantine boron, arrived at very different results from those of H. Deville and Wöhler. This chemist found that the black crystalline plates do not contain carbon, that their composition may be represented by the formula AlB_6, and that they contain 17 per cent. of aluminium. They can only be obtained by reducing boric acid with aluminium in crucibles of refractory clay at the temperature of melting iron. He found the crystals to dissolve in boiling nitric acid, and their density was 2.5345 at 17.2°. The yellow or brown octahedrons, he states, contain normally 3.8 per cent. of carbon and 13 per cent. of aluminium. Hampe regards the percentage of aluminium too high to permit of the supposition that this element is an impurity. He represents the composition of the crystals by the formula $C_2Al_3B_{24}$. They are formed when boric acid is reduced by aluminium, in crucibles of carbon or graphite at a higher temperature than that at which the black crystals are formed.

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[1] Annalen der Chemie, **183**, 75.

There is thus a disagreement in the statements of H. Deville and Wöhler and those of Hampe. The former regarded the yellow crystals as consisting of boron with variable proportions of carbon and aluminium, the latter regards them as a definite compound. The former thought the black crystals were the same as the yellow, only impure by their large percentage of carbon. Hampe states that the black crystals contain no carbon, but are composed of boron and aluminium only.

A. JOLY has undertaken to clear up the subject. He states that at the elevated temperature at which Deville and Wöhler worked only very small quantities of the large black crystalline plates were obtained. He finds that they are rarely formed when the temperature is at its maximum, but much smaller black crystals, united to the yellow ones, are formed if a small quantity of material is taken and the heating continued for a longer time. It is this substance which Deville and Wöhler probably analysed, while Hampe reduced boric acid in clay crucibles at a much lower temperature and obtained large black crystals which did not contain carbon. Joly also finds that the yellow crystals, AlB_6, dissolve readily in boiling nitric acid without leaving a sensible residue, but if the brown or black crystals obtained at a higher temperature are treated with this reagent, they are only partially dissolved, a carbonaceous residue remaining.

The reduction products of boric acid by aluminium are therefore as follows:

1st. The boride AlB, occurring in yellow hexagonal plates, studied by H. Deville and Wöhler.

2d. The boride AlB_6, occurring as large black crystalline scales.

3d. Yellow cubical crystals, containing carbon and aluminium.

4th. A carburet of boron, or probably several carburetted products, produced, in the presence of carbon and an excess of boric acid, at an elevated temperature by the transformation of the preceding products.—(*Comptes Rendus*, 97, 456.)

E. H. K.

Samarium and its Compounds.

This element was discovered by Lecoq de Boisbaudran in samarskite about 1878. Since then considerable doubt has existed in regard to its nature, and for a time it was thought to be identical with the decipium of Delafontaine. The properties of the element have now been carefully studied, and its atomic weight determined by P. T. Cleve. The raw material used for extracting the oxide of samarium consisted of a mixture of almost all the rare oxides of the earth metals derived from orthite found at Arendal in Norway. The mixture of earths was treated with nitric acid and heated until it began to give off red vapors. After cooling, the mass was treated with water, which left undissolved a large quantity of basic nitrates, principally of cerium and thorium. After washing, the basic salts were mixed with strong sulphuric acid, and the solution of the sulphates in cold water was precipitated with large quantities of hot water, by which operation most of the cerium was separated as basic sulphate.

The solution was then precipitated with caustic soda, and the hydrate, principally of thorium, dissolved in dilute sulphuric acid. On evaporating, large bulky masses of thorium sulphate were obtained. The oxides which remained in the mother liquors were transformed into nitrates and added to the solution of nitrates obtained by the first operation. These nitrates were evaporated and the residue heated until red vapors were given off. On treating with water, a solution free from cerium and thorium was obtained.

The solutions free from the oxides of cerium and thorium, or containing only small traces of these oxides, were precipitated with potassium sulphate with the view of separating the cerium and yttrium oxides, of which the former were (incompletely) precipitated and the latter (incompletely) retained in solution.

The yttria earths (about 700 grams) were transformed into nitrates and subjected to the usual melting process, for the separation of erbia, from yttria, terbia and didymia. The basic nitrates thus obtained contained also a very small quantity of thulium, some erbia and ytterbia, and a considerable portion of holmia. The fractions containing yttria and didymia were saturated with potassium sulphate, and this precipitate was added to the similar precipitate formerly obtained. These difficultly soluble double sulphates were decomposed with boiling potash-ley, and the hydrates dissolved in diluted sulphuric acid were again treated with potassium sulphate. The precipitate was converted into nitrate and evaporated. The residue was heated to partial decomposition in order to separate the last remaining traces of thorium and cerium.

The soluble nitrates thus obtained, which contained principally didymium and lanthanum, but also samarium, terbium, yttrium, etc., were mixed with impure didymium, and then subjected to partial precipitation with cold dilute ammonia. The last fractions contained much lanthanum, which was separated partly by the Mosander method and partly by precipitation with ammonia. The first precipitations were treated with dilute ammonia. In this way several fractions were obtained, containing both terbia and didymia (samarium, etc.) They were again treated several times with sulphate of potassium.

The slightly soluble double sulphates were now decomposed, and the solution of the hydrates in nitric acid was repeatedly precipitated with ammonia. Six fractions were obtained; one of these consisted of about 67 grams of light-colored oxides, which gave the spectrum of samarium, and also that of didymium. This was treated with dilute ammonia until the spectrum of didymium was completely eliminated.

The pure oxide Sm_2O_3 was converted into sulphate, and as a mean of six closely agreeing experiments the atomic weight was found to be 150.021, or in round numbers 150. In the calculation the composition of the oxide is assumed to be Sm_2O_3. As to its position in the system of Mendelejeff, the author thinks it may most probably be placed in the 8th group on the 8th line where there is a gap for a group of unknown elements.

The salts of samarium are distinguished by a peculiar spectrum composed of several bands, four of which in the blue part of the spectrum are most characteristic.

Besides the oxide, the following compounds were prepared and analysed:

Chloride of samarium, $SmCl_3 + 6H_2O$.
Chloroplatinate of samarium, $SmCl_3, PtCl_4 + 10\frac{1}{2}H_2O$.
Platinocyanate of samarium, $2Sm(CN)_3 + 3Pt(CN)_2 + 18H_2O$.
Nitrate of samarium, $Sm(NO_3)_3 + 6H_2O$.
Acetate of samarium, $Sm(C_2H_3O_2)_3 + 4H_2O$.
Sulphate of samarium, $Sm_2(SO_4)_3 + 8H_2O$.
Selenate of samarium, $Sm_2(SeO_4)_3 + 8H_2O$.
Oxalate of samarium, $Sm_2(C_2O_4)_3 + 10H_2O$.

The salts of samarium agree closely in composition with the didymium salts, and of all elements samarium is most nearly related to didymium, less closely to the yttria metals, the platinocyanates of the latter being wholly different from the samarium salt, which resembles the corresponding salts of cerium, lanthanum and didymium.—(*Journal of the* (*London*) *Chemical Society*, 1883, 362.)

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